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POSSIBLE CAUSES OF THE VOLCANIC ACTIVITY AT LASSEN PEAK.*

BY

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My appearance before you to-day is due entirely to your watchful Secretary, who has discovered me searching for an earthquake within the boundaries of California and has very promptly summoned me to give an account of myself before this body. He has also asked me, very pertinently, to explain what I proposed to do with the earthquake in case I found it. It is a fair question.

Most of you will recall that on Memorial Day, in the year 1914, Lassen Peak broke out into activity with an explosion of ash-laden steam within the summit crater, which was witnessed by a number of people. Forest rangers climbed the mountain next day and found there, inside the old crater bowl, a small explosion-vent some 40 feet long and 25 feet wide with two cracks extending east and west from the opening to a distance of a hundred feet or more. The crater bowl was oval in shape, ten to twelve hundred feet in diameter, about 350 feet deep from the bottom to the highest point of the rim, and was rarely free

* An address delivered before the Commonwealth Club of San Francisco on July 21, 1922.

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from snow at any season of the year. In the winter time the accumulation of snow usually amounts to 30 or 40 feet, which does not melt to any considerable extent at this elevation (10,466 feet) before the middle of May. The explosion was followed by considerable steaming, and the rangers noted streams of water from the melting snow pouring into the small explosion vent and the cracks extending out from it. Very little attention has been paid to these two cracks by anyone who saw them or who has since learned of their existence. I shall ask you, however, to bear these in mind, for they have much to do with the search for the earthquake for which I am to account to you.

Other explosions followed this one at intervals of two or three days throughout the summer and autumn, increasing gradually both in duration and intensity. Many of the more powerful outbreaks lasted for four or five hours and steam clouds, black with ash, rose to a height of 10,000 feet or more above the summit. The country roundabout the mountain was strewn with ash and stones up to a foot or more in size for two or three miles. These rested on the snow during the early eruptions, and as long as the snow lasted, showing that they were quite cold at the time when they were thrown out. In the winter season following, no very accurate record was kept of these occurrences, for the mountain is shrouded in cloud and snow during that season and is often invisible for periods of several days or weeks.

The explosion vent grew in magnitude during this interval until it included nearly all of the old crater bowl. An ascent over the snow in March of 1915 showed a hole nearly a thousand feet in diameter, with steam emerging at several points, notably at the west end, where there was a notch in the rim toward which one of the two original cracks had been directed.

This gradually increasing activity culminated on the night of the 19th of May, 1915, almost exactly a year after the first eruption, in a terrific outbreak, followed by a mud flow on the northeast slope of the mountain, which devastated the valleys of Hat Creek and Lost Creek for some twenty miles.

It was on this evening also, about nine o'clock, when the only authentic appearance of red-hot rocks was noted. Mr. J. R. Milford and a party of friends were watching the volcano from the windward (west) side, which was the only direction from which it was clearly visible on that night. Mr. Milford has given

a very graphic description of the glow at the top of the mountain illuminating the great cloud, and the gradual appearance of a red line marking the notch in the crater rim on the west side, which grew in intensity until the crater seemed to overflow like a great pot of slag forming momentary trails of red down the western slope of the peak. This operation he saw several times repeated between the hours of nine and ten, after which the activity diminished until it was no longer visible.

Closer inspection of this side of the mountain afterward does not verify all the details of Mr. Milford's description, though there is no doubt that he saw glowing material at the summit and the glow on the clouds. There is no appearance of flow structure in the lava which now fills the western notch, and furthermore at the temperature of red heat this lava is solid, not liquid. It was therefore not a lava stream which he saw, but the volcano plug itself thrust upward into the notch as a result of the pressure from below, during which red-hot material, though still solid, was exposed. The breaking up of these hot rocks and the fragments which rolled down the mountainside gave to Mr. Milford the impression of flow movement at a distance of twenty miles.

Notwithstanding the spectacular character of this appearance of red-hot lava and the tremendous explosions with which it was accompanied, this was not the most conspicuous effect of the night's activity. On the northeast slope of the mountain a mud flow developed which passed down Lost Creek and over the divide into Hat Creek, then following and laying waste both valleys for twenty miles or more to the northward. Newspapers and contemporary publications represented this mud flow to have come directly out of the crater, but this was not the case. Mr. B. F. Loomis, of Viola, one of the keenest observers of the mountain during this period, states this case briefly and succinctly:

"I do not believe that any hot water poured out of the crater as such at any time. Of course not. It is unthinkable that water, either cold or hot, would flow over the crater rim in gentle ripples while hot rocks and mud bombs were being hurled into the air a mile."

More deliberate observation afterward reveals the fact that the first evidences of the mud flow occur about 1500 feet below the summit. Here, in a bay of the mountain, there was stored up from the previous winter, a mass of snow and ice which is

never completely melted in a normal year. Its depth has been variously estimated at from 50 to 100 feet. With such a mass of snow upon which the condensed steam and hot ash from the fearful explosions of that night fell, abundant material was furnished for an avalanche down Lost Creek Valley from 10 to 20 feet in depth.

Still, such an avalanche of mud and water, fearful though it was, would not have created the devastation afterward found there, without the release of forces of even more awe-inspiring magnitude. The Forest Service estimates that five million feet of primæval forest timber stood in this valley before the eruption of May 19th. Afterward it was completely gone, not a stump or root or trace of snow remained to indicate what had been on the valley floor before this eruption. Indeed the trees were removed for some hundreds of feet above the uppermost limit reached by the flood.

There is only one agency competent to account for such complete devastation, and that is a horizontal blast from the crater itself, shot directly into this mass of timber and snow. Furthermore, there is abundance of direct evidence of the progress of this blast, for on the sides of the valley far above the boundaries of the mud flow, trees are down which were not removed, and they lie without exception with their tops pointing straight away from the crater in spite of the fact that they lie upon steep hillsides. Not only this, but every tree has been subjected to a terrific sand-blast, which has carried away the bark on the side toward the volcano while it remains undisturbed on the protected side. Trees which are broken off instead of uprooted have left behind stumps completely rounded off by the blast, and grains of volcanic sand have been driven into these trunks for an inch. These corridors of parallel tree trunks extend for nearly two miles on both sides of the valley far above any point reached by the flow of mud.

It could also be observed in the weeks following this eruption that the foliage of the standing trees on the borders of the devastated area was singed by the heat of the blast. Farther on in the region beyond the mouth of the valley, where the blast had spent its force, all the foliage was brown for a half mile or more.

Notwithstanding this no fires were kindled, which would seem to indicate plainly either that the blast was momentary or that its temperature fell somewhat short of the temperature necessary to

kindle even dead twigs. Probably both of these conclusions are justified.

The total extent of the blast was about four and one-half miles in a direct line from the mountain summit, and the width of the zone of complete devastation was about a mile and a quarter at its widest point. Notwithstanding this catastrophic outburst there was no eye-witness of the occurrence of any of these phenomena. It happened at night and the first evidence of it to reach the public came in a telegram from the forest ranger stationed on Hat Creek, several miles below, who reported a devastating flood of milk-warm water and mud which was covering the meadows in the northern reaches of Hat Creek Valley, carrying away outbuildings and rendering the cattle ranches uninhabitable. Fortunately the number of persons in the valley thus early in the season was small and no live stock had yet been brought in, so that no actual loss of life occurred, but it is safe to say that if a city had been located in Hat Creek Valley at the point where it came under the direct power of the blast, as was the case in the great eruption of Mt. Pelée in Martinique (1902), the loss of life might have been as complete as it was then.

Following this outburst the volcano remained active more or less continuously during the next three days, being shrouded in smoke and difficult of observation during most of that period. At five o'clock on the afternoon of the 22nd came the greatest eruption of all, in which the volcano cloud rose to a height of more than five miles and could be plainly seen for a hundred miles or more in any direction. This was the culminating outbreak of the entire period of activity. Since that time the explosions have diminished gradually in violence until 1918, when they ceased entirely.

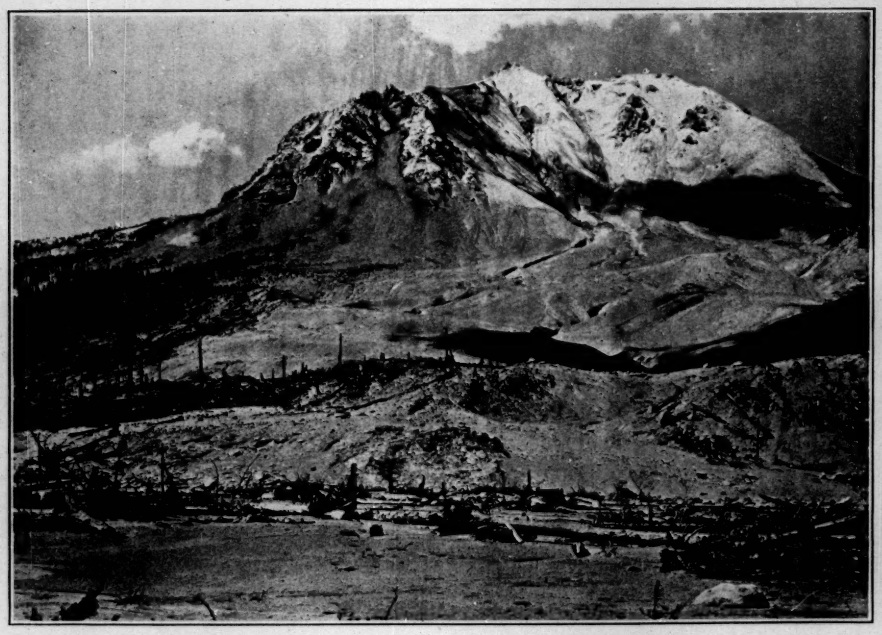
This culminating eruption of May 22, 1915, was also accompanied by a horizontal blast bursting from the same opening and proceeding in nearly the same direction as the previous one. The snow and the trees having been carried away for the most part by the first blast, less water and mud were available for the second flow, and practically no fresh damage was done. On the north slope of Lost Creek Valley a number of trees which had escaped the first blast were laid down like the earlier ones in parallel rows directly away from the crater, regardless of the lay of the land. In both of these blasts boulders up to 15 or 20 tons in weight

were dislodged from the top of the mountain and borne by the flood into the valley below, some for a distance of five or six miles.

The mechanism of these horizontal blasts is interesting. At the beginning, or shortly before the activity of the 19th, the crater floor was raised from below until it stood nearly level with the crater rim, a vertical movement of more than 300 feet. Had it gone higher the plug would undoubtedly have been dislodged from the vent entirely, and a flow of lava would have resulted. As it was the enchained pressure of volatile matter (mainly water) within the mountain appears to have found vent on the 22nd without actually blowing off the top of the mountain, and thereafter to have remained powerless to open the main crater conduit. It was as though the lava plug with which the volcano had remained sealed for so many years had been started upward by pressure from within which had then found release at the weakest point in the inclosing chamber. This happened not to be through the plug itself but below the plug on the northeast side of the mountain, much as a gas explosion in a kitchen stove might do, raising the lid and escaping in a horizontal blast from beneath it. After the emergence of these horizontal blasts the pressure was released and the lid collapsed. Its present appearance indicates rupture by such forces at a great many points of the exposed surface.

The mechanism of this entire sequence of volcanic activity can, I think, be inferred quite simply from the phenomena which have been described to you, and an appropriate application of the laws of physical chemistry. The great volcanic clouds, which characterized the explosions, were mainly of dust-laden steam. There is extremely little evidence of the participation of sulphur or other chemically active ingredients from beginning to end of this series of outbreaks. This will serve to establish the fact that no heat arising from chemical action within the volcano contributed to the reactions which occurred. This conclusion is supported by the further observation that, with a single minor exception, no fires were kindled by the blast, and, with the exception of the night of the 19th of May, 1915, no evidence of red heat was visible on the top of the mountain. Compared with other volcanoes which have been studied the volcanic phenomena at Lassen Peak occurred at comparatively low temperatures, certainly not above red heat. Also it should be noticed that Lassen Peak is located in a region of considerable rainfall, that the summit crater is almost never

FIG. 1.



View of Lassen Peak from the northeast showing the devastated mountainside together with the upper valley of Hat Creek and Lost Creek taken from a point between four and five miles from the summit, July 22, 1915.

free from snow, and that several streams of considerable size have their sources high on the flanks of the mountain. We are therefore dealing with a cooling volcano hearth in a region of abundant water supply.

Considering such dynamic systems, it is usual to assume that temperature and pressure rise and fall together. If the temperature were to rise the pressure would be increased, and if it were to fall the pressure would fall with it. In such reasoning, however, we overlook a vital factor in the consideration of silicate systems in the presence of considerable quantities of water. Laboratory measurements have shown that silicate solutions (rock magma) of high silica content easily take up ten or fifteen per cent. of water when in liquid condition under pressure and carry it in solution. In accord with this we also find in nature occasional pitch-stones and obsidians, which have cooled from the magma without crystallization, also containing 10 per cent. or more of water. On the other hand, crystalline rocks, as shown by the thousands of analyses made of them, contain no more than 1.5 per cent. of water. In order to crystallize, therefore, a high-silica magma, containing 10 per cent. of water, must divest itself of more than 80 per cent. of this water in the process of crystallization. Such a large proportion of the water content set free in the hot volcano chamber will increase the pressure enormously, even though the crystallizing operation is a cooling process.

By way of illustration of this, silicate mixtures have been prepared in the laboratory, inclosed in bombs with a sufficient quantity of water, and the pressure measured over a series of falling temperatures. It has been demonstrated, for example, that a simple mixture of silica, potash and water, which begins to crystallize at 500° C., will discharge this water when the temperature is lowered from 500° to 420° and the water thus set free will immediately develop a pressure appropriate to that high temperature. In this system the pressure may increase seven-fold (from 50 atmospheres to 340 atmospheres) in cooling through this interval of 80 degrees.

Without going further into the physico-chemical details, this process finds direct application at Lassen Peak. The magma is an andesite, high in silica, and so far as we have evidence of the heat conditions it is in process of crystallization at a comparatively

low temperature. The available water in the region is abundant to support the assumption that the percentage of water carried in the magma is large. The enormous quantities of water given off in the 300 or more explosions of record, some of which continued for several hours, still further support this assumption. The increase of water pressure depending upon the progress of crystallization is therefore appropriate to explain such a long series of explosions.

If this exposition has been clear Lassen Peak has been shown to be a true volcano and not a geyser, as sometimes asserted, that is to say, a chamber in which liquid magma (lava) is gradually crystallizing, located in a region which supplies to it an abundance of water. All of the explosions were steam explosions to which was added only the dust carried in the conduit or generated by attrition during the explosions. It is therefore from the engineering standpoint a cooling system to which no new energy is being supplied through chemical action of the kind which is characteristic of the volcanoes of Hawaii or of the Mediterranean.

It has been shown by laboratory experiments, in which all the factors were strictly measurable, that a silicate solution (lava), when crystallizing, sets free all of its water content above one or two per cent., and this water discharged in a closed chamber at a temperature of 600 or 700 degrees generates an enormous pressure within the chamber which may be sufficient to burst its bounds at the point of greatest weakness.

It remains to consider how such a process can produce a succession of explosions of gradually increasing intensity up to a culminating point and then gradually subside.

It is at this point that I wish to recall to your attention the two cracks in the crater floor which were discovered by the Forest Rangers shortly after the very first explosion at the summit. Considered as an explosion, this first outbreak was insignificant and not by any means adequate to explain the cracks. Still less are we able to recognize in it the outburst of 200 years of gradual crystallization and consequent accumulating steam pressure following the process above outlined. Such cumulative stresses should have been sufficient to blow off the top of the mountain, as once happened at Bandai San in Japan and at Katmai in Alaska. Suppose, however, that the temperatures within the mountain were relatively low, as every indication during the

period of explosive activity seems to establish, then crystallization was probably proceeding at a very slow rate in a magma of high viscosity which very probably was much undercooled. By that I mean that the liquid magma was so inert that crystallization was lagging, although it had already reached a temperature considerably below that at which crystallization would have occurred under more favorable conditions. Suppose further that into this inert mass there was suddenly introduced, through cracks at the top, a body of water, under a pressure head appropriate to the height of the mountain, which was speedily transformed to steam, which, under such circumstances, we know is quickly absorbed by the magma. The first effect of such an intrusion is to cause a considerable increase in the fluidity of the lava, and this in turn a considerable increase in the rate of crystallization. Water is coming in at a low pressure from one source, and in consequence of it water is released from another source (out of solution) at a high pressure. An increased rate of crystallization means an increased rate of setting free of the water content already impounded in solution in the inert lava. The resulting pressure increase might be expected to seek an outlet through the opening which had thus been broached in the crater floor, and a small explosion might result. An undercooled lava system, though inert if cool enough, is unstable, and once it is set in action through local increase of fluidity in this manner, the tendency to reach equilibrium (through crystallization) is strong. Consequently the action here indicated is likely to proceed rapidly and the rapidly accumulating pressure to find relief in successive explosions depending for their magnitude and frequency directly upon the rate of advancing crystallization and the increasing amount of participating magma as the successive explosions expose greater masses to the new and favorable conditions. This seems to me to account well for the low intensity of the initial outbreak and the gradual increase in volume and intensity as the crater floor was shattered by successive explosions and greater quantities of water were admitted to the volcano hearth, bringing an increasing quantity of crystallizing magma into an action which eventually becomes more or less self-perpetuating until all the available uncrystallized magma is participating. Then follows the culmination and subsidence.

This analysis, if correct, might lead to two alternative results. That the potential activity (pressure) within the mountain is due

to advancing crystallization, appears to be logically grounded and established by appropriate laboratory experiments. It could find release only in the breaking down of the resistance of the containing envelope, that is, the mountain itself. This might happen either from without or from within. If the release had come solely through accumulated pressure within, which eventually became adequate to overcome the normal resistance of the mountain, then a terrific explosion must have resulted through which the entire accumulation of energy would have found release in a single catastrophe. This obviously was not the case. If, on the other hand, the resistance of the mountain to the accumulated pressure within had somehow been weakened slightly by action from without, such as an earthquake crack, and this development of structural weakness had been followed by a succession of explosions extending it gradually, then we would seem to reach the counterpart of the present phenomenon.

It is for this reason that your Secretary found me searching for a record of an earthquake in California, one that occurred in April or May of 1914. Lassen Peak region is subject to earthquake disturbances, often of very noticeable magnitude, but no record exists of these local disturbances, either of their intensity, their direction, or their probable origin. So far as any records now available are concerned, we may not know whether the local earthquakes are to be regarded as possible causes or as effects of volcanic activity. For this reason I have been unable, so far, to verify my hypothesis fully, though I entertain no doubt of its substantial correctness, even without the record.

Speaking before the Commonwealth Club I feel free to emphasize our lack of knowledge of California earthquakes, for it was in this body, less than a year ago, that resolutions were passed urging a systematic study of the earthquakes of the west coast. It is probable that the need for such information in connection with volcanic activity at Lassen Peak will not impress you as a conspicuous and tangible need when compared with the need which is felt by engineers in the consideration of such problems as the proposed viaduct across San Francisco Bay, or the construction of buildings in regions peculiarly exposed to earthquake disturbance, or in connection with the water supply of our great cities, which, on this coast, frequently has to be drawn from the mountains many miles away. These are vital problems in California, and it

is a pleasure to see that this representative body stands ready to defend them as such. Anything less than systematic study and record is of little value in considering earthquake phenomena, as I will illustrate to you in a moment.

As a beginning of such study it will be interesting to you to know that on July 1st the U. S. Coast and Geodetic Survey began a new primary triangulation to extend from points on San Francisco Bay to Reno, Nevada, with the definite purpose of ascertaining whether or not there is a northward creep of the coastal region such as has been reported probable by the astronomers at Ukiah and at Lick Observatory. It is of the utmost importance to establish definitely whether there is such a creep or is not. For if the creep exists, and by its northward movement sets up a strain in the earth's crust, and if this crust when strained to the limit ruptures, producing earthquakes like that of 1906, then it is of the utmost importance that we should know the direction and rate of this drift, that we should know where the lines of weakness are located, where previous ruptures have occurred, which of these continue to be active and which are no longer so. This a primary triangulation will reveal.

It will interest you further to know that the U. S. Geological Survey, in coöperation with the Universities at Stanford and Berkeley, the Branner Society in the south, and the Seismological Society of America, whose President, Professor Willis, is with us to-day, have already been at work throughout the year gathering together information about these breaks or faults with the purpose of publishing a map showing where they are. These are the zones of mechanical weakness which, when they approach our large cities, are of the first economic importance.

There is also being built in Pasadena, through the courtesy of the California Institute of Technology, a new instrument designed especially for the purpose of studying local tremors and land slips. No such instrument, for the purpose of locating nearby disturbances of this kind, has been devised hitherto. If it proves successful the plan is to establish a number of stations equipped with them, through which to locate very exactly the direction of slips or tremors, and so to know not only the lines of weakness along which such disturbances may be propagated, but also the points of origin from which they may be expected.

You will recall the effort which was made in 1907 by the

California Earthquake Commission, in collaboration with government agencies, to obtain this information after the earthquake of 1906, but the surveys which were then made did not tell us positively either the direction or the magnitude of the displacement which had occurred, because the base-line then chosen was within the zone of the crustal creep, if there was one, and the consequent strain, and therefore within the zone affected by its release. Recognizing these limitations in the earlier effort, it is our hope and purpose not to be found short-sighted again. The astronomers are continuing their observations with additional instruments and, when supported by these surveys of the highest precision, which we hope may be continued for several years, we expect no movement within the coastal plain from Ukiah Observatory to the Mexican boundary to occur without our being able to ascertain precisely its direction, its magnitude, and its probable point of origin. It is my hope that the interest which has been shown by this most influential body in the inauguration of these studies and measurements by the Carnegie Institution of Washington and the scientific bureaus and institutions associated with it, may continue throughout their progress.

To emphasize to you the futility of personal evidence, as opposed to competent instrumental records, it may interest you to know that for a short time I thought to have found precisely the earthquake which I sought. A mining engineer, who was prospecting for values in the vicinity of Lassen Peak during April of 1914, assured me that he both felt and saw a considerable shock from his position a few miles to the east of the mountain, and that this disturbance proceeded visibly in the direction of the volcano crater itself. This direction of progress was also consistent with the general faulting of the region and therefore seemed to fulfil my expectations completely. But I thought best to inquire how he managed to see the earthquake as well as to feel it, and was told that it could be plainly followed by the thin line of dust cloud which marked its progress toward the mountain.

A short time afterward when I happened to meet my old associate in Lassen Peak exploration, Mr. Roy Sifford, who for twenty years has spent at least half of each year at the foot of the mountain, I took advantage of the occasion to ask him what the snow conditions were in the month of April within say

twenty miles of Lassen Peak. He replied at once that I could count on from five to six feet of snow at any point within twenty miles of Lassen at that time of the year. Just how it should be possible to observe an advancing dust cloud through six feet of snow was a puzzle which had the immediate effect of discouraging my interest in this particular evidence, and so my hope of completing the chain of circumstances which should explain the inception of volcanic activity at Lassen Peak in 1914 vanished. Perhaps I may yet be successful enough to find a more trustworthy clue. However that may be, this will serve to explain to you why I sought an earthquake in California this summer and the disposition which I proposed to make of it if found.

I thank you for your kind attention.

Manufacture of Vanillin by Electrolysis.—In the spring of 1897, a German patent was issued for a process for producing vanillin by subjecting isoeugenol to an electric current, the vanillin being formed by oxidation and appearing at the anode. The process was described in some detail, consisting essentially in placing in the anode cell a 15 per cent. solution of isoeugenol in an excess of sodium hydroxide, the cathode cell being charged with a 15 per cent. solution of sodium hydroxide. A current of about 5 volts and 6 amperes was recommended. The course of the action is followed from time to time by withdrawing small portions and testing for vanillin. A temperature of about 60° C. is advisable. When the action has progressed well, the anode liquid is shaken with ether which dissolves the vanillin and any unchanged isoeugenol. The vanillin is recovered by shaking with acid sulphite, and this compound decomposed in the usual way.

Notwithstanding the specific claims of this patent, Alexander Lowy and Catherine M. Moore, of the Department of Chemistry, University of Pittsburgh, found by careful experiments that the results stated cannot be obtained. Their work was communicated at the forty-second general meeting of the American Electrochemical Society in September last. All attempts to get an appreciable yield of vanillin failed. Vanillin, itself, was found to oxidize readily, and even if produced in the process will be at once converted into other substances. Experiments were also carried out in which sulphuric acid was used as the electrolyte, but also failed. In all the experiments a resinous substance was obtained. Statements are made in text-books that vanillin can be obtained electrolytically from isoeugenol, but such statements are not borne out by the investigation. If isoeugenol can be so converted, it must be under conditions different from those called for in the patent. H. L.

SCATTERED X-RAYS IN X-RAY PHOTOGRAPHY.*

BY

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WHEN matter is traversed by X-rays, it becomes the source of secondary X-rays. Part of this secondary radiation is of a fluorescent type, of longer wave-length than the exciting rays and, in general, less penetrating. The wave-lengths of the fluorescent radiation have usually been considered to be characteristic of the chemical element emitting them, although Compton [1] has observed evidence of a general fluorescent radiation whose quality is determined by the primary beam of rays and is independent of the material of the radiator. Another part of the secondary radiation consists of scattered rays, whose wave-lengths are the same as those of the primary beam and are independent of the character of the substance emitting them.

In elements of high atomic weight, the secondary radiation consists largely of characteristic rays; in substances of low atomic weight, the characteristic radiation is negligible, the secondary radiation being largely or entirely scattered radiation. Since the human body is composed almost wholly of elements of low atomic weight, it is the scattered type of secondary radiation which is of chief interest in the application of X-rays to the diagnosis and cure of disease.

The present studies were carried out for the purpose of finding the essential facts about scattered radiation as it occurs in making X-ray photographs of the human body, with the object of determining the best method of avoiding its harmful effects upon the quality of the radiograph. The X-ray image is a shadowgraph formed by the primary rays from the focal spot of the X-ray tube; the differences in optical density in the various parts of the radiograph are produced by the differences in absorption of the rays by the various portions of the subject. The scattered radiation reaching the photographic surface diminishes the contrast and detail, rendering the radiograph less valuable for diagnostic purposes.

* Communicated by Dr. C. E. K. Mees, Director of the Laboratory and Associate Editor.

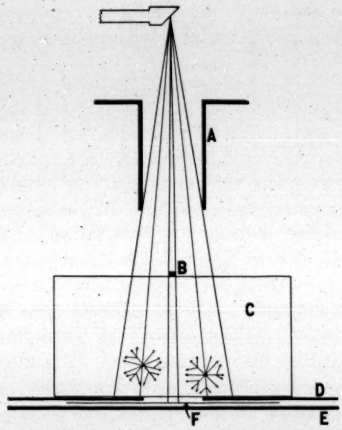
Matter is not transparent to X-rays but rather translucent. If the eye were sensitive to X-rays, human tissue when illumined by X-rays would appear to consist of a vapor-like substance. It would resemble more a milky solution than a clear solution. Making an X-ray photograph of a part of the human body is similar to making a photograph of a building through a fog; the parts of the building nearest the camera would appear the most clearly in the photograph and distant portions less clearly or not at all; only the larger outlines would be visible; the finer structural details would be either indistinct or invisible, and the whole photograph would exhibit such lack of contrast and detail as to render it a very unsatisfactory picture. Such is the case with ordinary radiographs of the thicker portions of the human body, and as long as there was no remedy for the effects of scattered rays, we had to be satisfied with such radiographs as could be obtained.

Previous experimental work on X-ray scattering has dealt mainly with the fundamental characteristics of the phenomenon. Only small volumes of scattering material were used in order to minimize extraneous effects such as absorption and rescattering of the scattered rays. The information obtained thus far is very incomplete; some of it is contradictory, and it is not possible to derive from it much knowledge of the behavior of scattered radiation in the relatively large volumes of matter encountered in medical radiography. Accordingly, in the present studies, direct observations were made on the scattered radiation occurring in large volumes of matter under the conditions of practical X-ray photography.

The effect of scattered radiation upon the radiograph depends upon the relative intensity of the scattered radiation and the primary image-forming radiation reaching the photographic film. The method of measuring the relative intensity of scattered and primary radiation is illustrated by Fig. 1. The scattering material *C* consisted of a volume of water contained in an aluminum tank. Water is very similar to human flesh in its absorption and scattering of rays and for that reason was used in nearly all the experiments. A small lead disk *B*, supported over the surface of the scattering material, served to absorb completely all the X-rays striking it so that its shadow on the film could be reached only by the scattered rays and the small amount of pri-

mary radiation coming from the portions of the tube outside the focal spot. Since all this radiation is diffuse in character, the radiation falling in the shadow of the lead disk B will be termed *diffuse radiation* while the image-forming radiation received by the film from the focal spot will be called *focal radiation.* The area of the film outside the shadow of the lead disk receives both the diffuse radiation and the focal radiation and it is possible by means of the film F to measure the ratio of the intensity of

FIG. 1.



the diffuse radiation (D) falling in the shadow of the lead disk to that of the total radiation (T) falling outside this shadow. The ratio of diffuse to total radiation, $\frac{D}{T}$, was first measured for various thicknesses of water and for various sizes of image as limited by the lead cylinder A. The Coolidge radiator type tube was operated at 60 kilovolts (effective) and the distance of the target (focal spot) from the film was kept at 20 inches. The tank holding the water was 12 inches square and measurements were made with thicknesses of water varying from 2 to 10 inches. In Table I are given the values obtained when the cone of rays emitted by the tube was sufficient to cover an area 20 inches in

diameter in the plane of the film. In column 2 are tabulated the observed values of $\frac{D}{T}$, the ratio of diffuse to total radiation, and in column 3, the values of $\frac{D}{F}$, the ratio of diffuse to focal radiation calculated by the relation

$$\frac{D}{F} = \frac{\frac{D}{T}}{1 - \frac{D}{T}}.$$

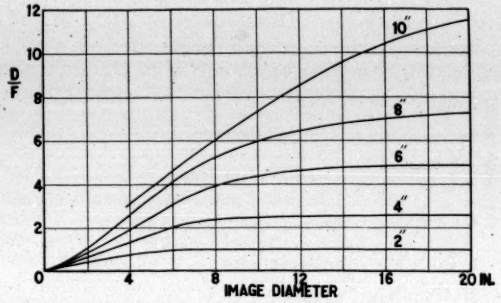
TABLE I.

Thickness of Water in Inches.	Ratio Diffuse to Total Radiation $\frac{D}{T}$.	Ratio Diffuse to Focal Radiation $\frac{D}{F}$.
2	.50	1.0
4	.72	2.6
6	.83	4.9
8	.87	6.7
10	.92	11.5

These values show the important rôle played by scattered radiation in practical radiography. In thicknesses corresponding to the thicker portions of the human body, the diffuse radiation is several times the intensity of the focal radiation which forms the image. These data explain why it is so difficult to get satisfactory radiographs of large patients; the scattered radiation blots out most of the contrast and detail that would otherwise be afforded by the primary rays. It is quite evident that the removal of the scattered radiation would produce a very marked improvement in the quality and diagnostic value of the radiograph. The most common method of reducing the intensity of scattered radiation has been to limit the volume of material rayed by means of a lead cylinder, cone or diaphragm placed between the X-ray tube and the patient. A series of measurements was therefore made to determine the efficiency of this method of removing scattered radiation. The results are shown in graphic form in Fig. 2, which shows the ratio of diffuse to focal radiation plotted against the diameter of the image on the film as determined by the circular diaphragm above the scattering material. The thickness of scattering material (water) is marked on each curve. The ordinate value unity marks the point where the diffuse radiation is equal to the focal radiation; the

fact that only a small portion of each curve lies below this value indicates the small range of conditions where the diffuse radiation is reduced to a lower intensity than the focal radiation and, furthermore, to achieve this result, the image must be diaphragmed to a rather small size. This method of reducing the scattered rays does have a limited application in practice; it is sometimes feasible to use a radiograph as small as 4 or 5 inches in diameter,

FIG. 2.



and diaphragming to this size produces an appreciable improvement, although it is not highly efficient in removing scattered radiation.

When scattered radiation is removed by any method the exposure must be increased to make up for the loss in total X-ray intensity. The use of a diaphragm between the tube and the scattering material does not affect the intensity of the focal radiation reaching the film; the loss in total intensity is that due to the decrease in scattered radiation and may easily be calculated from the observed ratio of diffuse to total radiation. If the standard exposure for any thickness be taken as that for a twenty-inch image diameter, the factor F by which the exposure must be increased when the image is diaphragmed to a smaller size is given by the equation

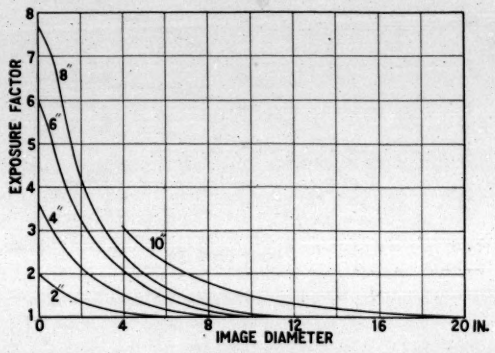
$$F = \frac{1 - \frac{D}{T}}{1 - \left(\frac{D}{T}\right)_{20}}$$

where $\frac{D}{T}$ is the ratio of diffuse to total radiation for the image size in question and $\left(\frac{D}{T}\right)_{20}$ is that for an image diameter of twenty inches. Fig. 3 shows the exposure factor as a function of image diameter for the various thicknesses of water.

Decreasing the voltage at which the tube is operated was found to diminish only slightly the proportion of scattered radiation reaching the film.

Another possibility that has been suggested for removing

FIG. 3.



scattered radiation is to insert between the scattering material and the film a filter which absorbs the scattered rays and transmits the primary rays. This suggestion is based upon the supposition that the secondary radiation is of softer or more absorbable type than the primary radiation. The ratio of diffuse to total radiation was therefore measured with several types of filters placed between the scattering material and the film. The results are tabulated in Table II.

TABLE II.

Filter.	Ratio Diffuse to Total Radiation.	Ratio Diffuse to Focal Radiation.
None	.83	4.9
1/16-inch aluminum	.82	4.6
1/8-inch aluminum	.80	4.0
.001-inch lead foil	.79	3.8

It is evident that filters are not very efficient in reducing the proportion of scattered radiation. Furthermore, what little advantage they have in this respect is counteracted by their selective absorption of the softer primary rays which give the greatest contrast in the image. Experiments showed that filters used in this way had no measurable effect upon radiographic contrast, their only effect being to increase the exposure.

The enhanced contrast produced by the use of intensifying screens with film has given rise to the suggestion that they owe this effect to a lack of sensitiveness to scattered rays. Measurements were made to determine whether this is the case. The values in Table III show how the proportion of diffuse radiation is recorded by intensifying screens as compared with plain film.

TABLE III.

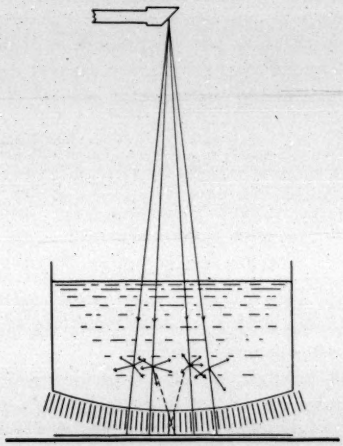
	Ratio Diffuse to Total Radiation.	Ratio Diffuse to Focal Radiation.
Plain film in cardboard exposure holder.....	.83	4.9
Plain film in aluminum cassette	.81	4.3
Single intensifying screen in aluminum cassette..	.80	4.0
Double intensifying screens in aluminum cassette..	.78	3.5

Measurements on two other types of intensifying screens gave substantially the same results as those above. It is apparent that intensifying screens do not effectively diminish the proportion of scattered rays recorded upon the film.

During the progress of these experiments, a description of the Potter-Bucky diaphragm was published.[2] This apparatus was perfected by Dr. H. E. Potter and consists essentially of a grid placed between the scattering material and the film, so designed as to allow the focal rays to pass through, but absorbing a large portion of the scattered rays. The grid is made of long strips of lead foil, as illustrated in the sectional diagram of Fig. 4. These strips are spaced equal distances apart by intervening wooden strips. The plane of each strip of lead is in line with the focal spot and the long dimension of each strip is parallel to the photographic surface. The focal rays pass through the slots between the lead strips; the scattered rays between a limited angle may pass between the strips; beyond this angle the rays are absorbed by the lead strips. In order to prevent the shadows of the lead strips from showing in the radiograph, the grid is

moved continuously during the exposure in a transverse direction perpendicular to the length of the strips while the subject radiographed, supported above the grid, and the film below the grid are kept stationary. The advantage of the Potter-Bucky diaphragm is that its effectiveness does not depend on restricting the size of the radiograph—a radiograph of any size can be made with it—and it is equally efficient in removing scattered radiation over each part of the radiograph. With this diaphragm, Doctor Potter was able to produce radiographs that

FIG. 4.



were far superior in contrast and detail to radiographs made by any other technic.

It was decided to make a quantitative study of the Potter-Bucky diaphragm to determine the effect of various factors in design upon its efficiency in removing scattered radiation and in showing fine radiographic detail. Instead of using a complete grid for this study, it was found advantageous to use a single element of the grid, a single slit, formed of thick lead and omitting the wood filling material. A six-inch depth of water in an aluminum tank was used as the scattering material as illustrated in Fig. 4. The X-ray tube was operated at 60 kilovolts

and the distance of the focal spot from the slit was kept at 25 inches. The ratio of diffuse to total radiation was measured for various widths and depths of the slit. It was found that the efficiency of the diaphragm in removing scattered radiation depended only on the ratio of the slit width to the slit depth and was independent of the absolute size of the slit. Fig. 5 shows relation between the $\frac{D}{T}$, the ratio of diffuse to total radiation, and $\frac{W_s}{D_s}$, the ratio of the width to the depth of the slit.

FIG. 5.

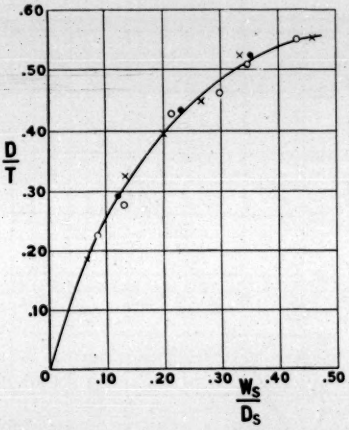


Fig. 6 shows the ratio of diffuse to focal radiation also as a function of $\frac{W_s}{D_s}$.

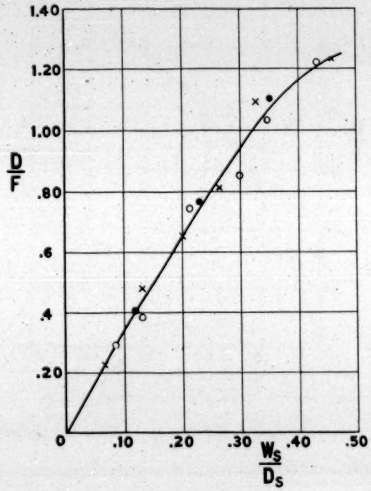
As compared with other methods, it is apparent that the Potter-Bucky diaphragm is highly efficient in removing scattered radiation. For instance, in a six-inch depth of water, a Potter-Bucky diaphragm with a slit ratio, $\frac{W_s}{D_s}$, of 0.2 is as effective in removing scattered radiation as a circular diaphragm above the water giving an image diameter of 1.5 inches, and the Potter-Bucky diaphragm cleans up the scattered radiation with equal effectiveness over the whole area of a full-size radiograph.

If we define the efficiency of a diaphragm as the fraction of the scattered radiation removed by it, for a six-inch depth of water the efficiency may be calculated from value of $\frac{D}{F}$ by the equation

$$E = \frac{4.9 - \frac{D}{F}}{4.9}.$$

Fig. 7 shows the efficiency of the Potter-Bucky diaphragm as a function of the slit ratio, $\frac{W_s}{D_s}$. Slit ratios of 0.25 to 0.17 or

FIG. 6.



less are entirely practicable and give efficiencies ranging between 80 and 90 per cent.

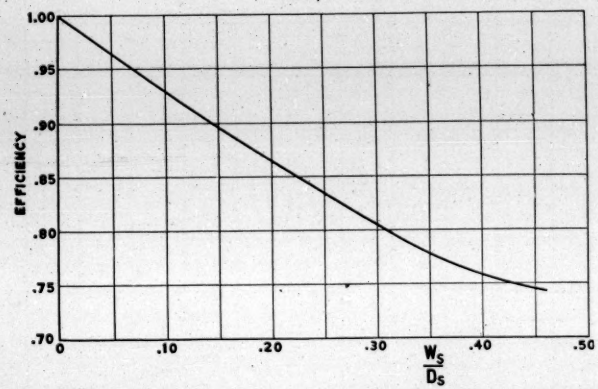
The exposure factor of the Potter-Bucky diaphragm is shown as a function of the slit ratio in Fig. 8

In a practical Bucky grid, the strips of lead foil are held apart in their proper positions by strips of wood. Measurements showed that the effect of these wooden strips upon the efficiency is almost negligible. The lead strips transmit some of

the scattered rays incident upon them and this factor also lowers slightly the efficiency in a complete grid. The exact effect of the transmission of scattered rays by the lead strips has not been determined but preliminary experiments indicate that the effect is not large.

The effect of the Potter-Bucky diaphragm in enhancing contrast in the radiograph depends upon the efficiency in removing scattered radiation. The definition in the radiograph is affected

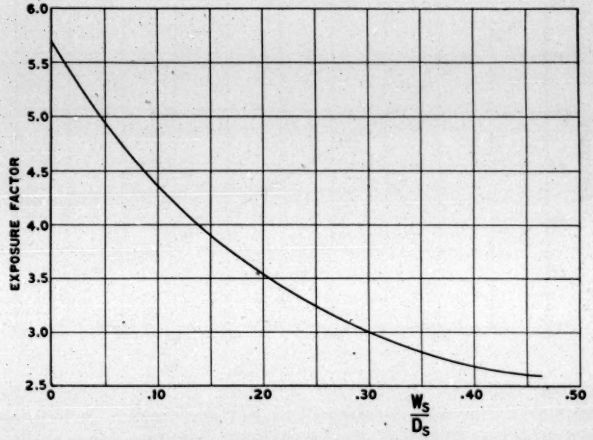
FIG. 7.



by an additional factor, the increased distance between the patient and the film necessitated by this diaphragm. It is to be expected that this increase in distance will, to some extent, counteract the beneficial effect of removing scattered radiation upon definition. This was found to be the case. The definition obtainable in radiographing through a scattering material was studied by means of a set of wire gauzes of various sized meshes immersed in the tank of water. The distance between the scattering material and the film was found to have a very marked effect upon the radiographic definition. If the distance between scattering material and film were too great, the definition was better without the diaphragm than with it. It was also found, for instance, that if the slit width were kept at a constant value of, say, 0.13 inch, and the slit depth diminished from 1.00 inch to 0.20 inch to permit a shorter distance between scattering material and

film, the definition was improved, although this procedure allowed more scattered radiation to fall on the film. With a six-inch depth of water and a distance of 0.7 inch between the water and the film, a slit ratio of 0.26 gave the same definition as was obtained without the diaphragm. Either a smaller slit ratio or a lesser distance between scattering material and film was required to gain an improvement in definition. When the distance between scattering material and film was as large as one

FIG. 8.



inch, the smallest slit ratio tried, 0.044, failed to give as good definition as was obtained without the use of any diaphragm. The advantage of the ordinary technic without the diaphragm in this case is that the subject radiographed is very close to the film. If, however, with the Potter-Bucky diaphragm the distance between scattering material and film is made sufficiently small, a marked improvement in definition is produced. To obtain high contrast as well, the ratio of slit width to slit depth should be small. The problem in grid design, then, is to make the grid as thin and fine-meshed as possible. Some clear space must be allowed above and below the grid to allow it to travel free from any friction caused by rubbing against the cassette containing the

film or the cover supporting the patient. This clear space should be reduced to a minimum and the thickness of the top of the cassette and the thickness of the cover of the diaphragm should also be made as small as possible, so that every precaution is taken to minimize the distance between patient and film.

As will be noted from Fig. 4, the grid has a curvature like the surface of a cylinder. If the film is held flat, the distance between scattering material and film is greater at the edge of the film than at the centre. In order to obtain the same excellence of definition over the whole area of the film, the curvature of the film should follow that of the grid, keeping the same distance between scattering material and film over its whole area. The use of a curved cassette for holding the film has been suggested by Van Allen,[3] who finds that it reduces both the distortion and fuzzy appearance (poor definition) which are characteristic of objects distant from the film.

It is often suggested that an additional improvement in the Potter-Bucky diaphragm would be obtained if the lead strips extended in both directions, forming a set of rectangular cells. The cellular grid is the design generally ascribed to Bucky's original invention. Experiments on the definition obtainable with small rectangular cells showed that for equal distances between patient and film and equal ratios of width to depth, the cells gave but little better definition than was obtained by the long slit. If it were possible to construct economically a cellular type of grid, so designed that it could be moved during the exposure as to avoid grid shadows upon the film, it would doubtless be of advantage. Other types of grid are readily conceivable, such as a flat grid with radial slits, or with one continuous lead strip bent in the form of a spiral. These could be rotated to avoid grid shadows instead of requiring a transverse motion. The trouble with such designs would be the difficulty and cost of construction which would scarcely be justified by the slight improvement they would afford. The present experiments indicate that the most practicable procedure is to push the Potter type of grid to the limit of its effectiveness.

To try out in a practical way the conclusions reached in this study of the Bucky diaphragm principle, a thin, fine-meshed grid was constructed. The grid was made 0.16 inch thick; lead-foil strips three-thousandths of an inch thick were spaced

at a distance of .026 inch apart by means of strips of celluloid. The curved frame in which the grid was mounted was fitted with an aluminum floor 0.02 inch thick to support the grid over its whole area. Some difficulty was experienced in getting the lead strips lined up properly, but after some adjustments a fairly satisfactory result was obtained. The cover of the diaphragm for support of the patient was of 1/32-inch aluminum mounted on a curved frame and the top of the curved cassette was also of 1/32-inch aluminum. When sufficient space was allowed for the grid to travel without friction, the total distance from the patient to film was found to be 3/8 inch. Probably by additional adjustments, this distance could be reduced slightly. In present commercial models of the Potter-Bucky diaphragm, the distance between patient and film ranges from 3/4 inch to 1 1/4 inches, and they are designed to take flat cassettes. Radiographs of several portions of the body showed clearly the advantage of the experimental diaphragm over the usual type of diaphragm in radiographic definition. The advantage of this diaphragm in giving sharpness of outline and fine structural detail was especially noticeable at the edge of the film where the curved cassette brings the film much closer to the patient than does the flat cassette employed with present commercial diaphragms.

Although there is still some room for improvement, the Potter-Bucky diaphragm in its most efficient form may be considered a very satisfactory solution of the problem of scattered radiation in radiography. Radiographs made with the diaphragm show a striking superiority in both contrast and detail over those made by the ordinary methods. The only disadvantage is the increased exposure required, necessitating increased precautions for immobilizing the part rayed and permitting fewer radiographs to be taken with safety to the patient. This disadvantage is inherent in any method of removing scattered radiation and the more scattered rays are removed, the greater must be the exposure required to compensate for the loss in total X-ray intensity.

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[2] POTTER, H. E.: *Am. J. Roentgenol.*, **7**, June, 1920, p. 292.
[3] VAN ALLEN, H. W.: *Am. J. Roentgenol.*, **8**, June, 1921, p. 340.

THEORY OF END-LOSS CORRECTIONS AND ITS APPLICATION TO UNIFORM, ELECTRICALLY HEATED TUNGSTEN FILAMENTS IN VACUO.*

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INTRODUCTION.

WITH the advent of metal filament, incandescent lamps, the existence of losses where the filaments are attached to lead-wires or come in contact with supports, became a matter of concern. The magnitudes of these end-losses, as they are called, were studied [1, 2] and means for reducing them as far as practicable were considered and employed.

The commercial investigation consisted of an adaptation of the optical pyrometry methods of pure science to the study of small incandescent filaments. In addition to yielding results of importance in lamp design, that work led to a broader study of materials at high temperatures from the viewpoint of pure science. In fact, the physical properties of many materials are studied with ease only in case they may be mounted in filament form and heated electrically. To obtain results in such cases applicable to uniformly heated portions of the material, consideration must be given to the end-losses resulting from the conduction of heat from the filament to the leads and supports.

End-loss effects may be eliminated (1) by selecting filaments that are so long that the corrections are negligible; (2) by taking difference measurements on filaments differing only in length; (3) by determining the corrections to be applied through a study of the variation in temperature and related properties near a cooling lead or support, or (4) by introducing devices which permit of measurements on uniformly heated portions of the filaments only. The device will depend upon the problem. In electrical measurements, small potential leads attached to the main filament at considerable distances from the cooling leads may be used; in thermionic measurements, a cylindrical anode

* Communicated by the Director of the Laboratory.

about the central portion of the filament, slightly separated from two others of the same diameter about the end portions, will serve.

In much work, computed end-loss corrections serve as satisfactory approximations. In fact, in case of initial imperfection or of accident occurring during the course of the work, computation may prove the only means of salvaging data and results

TABLE I.

Quantities and Symbols.

Symbol.	Quantity.
T	temperature.
i	filament current density.
ρ	resistivity.
σ	radiation intensity.
k	thermal conductivity.
r	filament radius.
l	distance along filament from junction.
b	filament brightness.
e	thermionic current density.
sub m	values occurring at centre of a long filament.
sub μ	values occurring at centre of short filament.
sub j	values occurring at junction of the filament with support or lead.
sub o	values corresponding to a "standard" operating condition in which $r = .01$ cm. and $T_m = 2400°$ K.
α	$\frac{T}{\sigma}\frac{d\sigma}{dT}$ ratio of percentage change in σ to corresponding percentage change in T.
β	$\frac{T}{\rho}\frac{d\rho}{dT}$ ratio of percentage change in ρ to corresponding percentage change in T.
δ	$\frac{T}{b}\frac{db}{dT}$ ratio of percentage change in b to corresponding percentage change in T.
τ	T/T_m, reduced temperature.
Q	$\sqrt{\frac{2\sigma_m(\alpha-\beta)}{k_m T_m}}$
P	Q/r, factor for obtaining reduced distributions.
L	Pl, reduced length.
w	width of filament.
t	thickness of ribbon filament.
Δl	effective filament shortening due to end loss.

obtained on materials originally mounted for study by methods (1) or (2). Moreover, once the corrections are determined accurately, this procedure may result in saving much time, for actual end-loss determinations are usually not simple.

This paper contains a method for computing end-loss correc-

tions and an application of it to the case of uniform, electrically heated, tungsten filaments in vacuo.

As previous work not already mentioned which serves as a foundation for the present paper, reference should be made to Worthing,[3, 4, 5] Langmuir,[6] and Stead.[7]

THE LONG FILAMENT.

Theory.—A long filament for this purpose is defined as one in which the cooling effects due to the leads or supports do not appreciably affect the temperature of the central portion. In contrast to the short filament, discussed later, the cooling effect at any point in a long filament is due only to a single lead or support.

Consider a long, uniform, electrically heated, cylindrical wire in vacuo, whose variations in resistivity, thermal conductivity, and radiation intensity with temperature are known. Assume the temperature variation over any cross-section so small that the surface values of the resistivity, etc., at any point may be taken without appreciable error as the average over the cross-section. In the ordinary metallic filaments used in lamps, this is closely realized. How closely this is the case is shown by the fact that in a 0.2 mm. tungsten filament, approximately that of the 500-watt, 110-volt tungsten lamp used previous to the advent of the gas-filled lamp, the greatest difference in temperature between axis and surface normally did not exceed a quarter of a degree.[3]

The fundamental equation giving, on the above assumptions, the temperature distribution near a cooling lead (see Table I) is

$$(1) \quad i^2\rho\pi r^2 dl + \left[k\frac{d^2T}{dl} + \frac{dk}{dT}\left(\frac{dT}{dl}\right)^2\right]\pi r^2 dl = 2\pi r\sigma dl.$$

The three terms in order represent, for an element of filament of length, dl, the rate of production of heat electrically within it, the net rate of conduction of heat into it through its ends, and the rate of radiation of energy from its cylindrical surface.

Equation 1, with conditions characteristic of long filaments introduced, leads finally to a form which may be evaluated to give the variation in temperature along the filament. Throughout a considerable part of the end-cooled length, the evaluation is best done graphically or algebraically. However, in the region where the temperature T is nearly equal to the central maximum temperature T_m, accuracy and ease of evaluation are brought about

by the close approach to the well-known exponential form for the temperature distance relation, in which

$$(2)\quad \left[\frac{dT}{dl} = \frac{Q}{\sqrt{r}}(T_m - T) = P(T_m - T)\right]_{T \doteq T_m}$$

or expressed integrally

$$(3)\quad \left[1 - \frac{T}{T_m} = e^{-P(l-l')}\right]_{T \doteq T_m}$$

Q is a combined function of several properties of the filament material each of which is a function of T_m only, r is the filament radius, l' an integration constant, and P a convenient abbreviation for $Q/\sqrt{r}$.

Once the curve giving the temperature variation in an end-cooled portion of a filament is platted, other curves giving resistivity, etc., variations may be obtained through their known dependencies on temperature.

For much that follows it is convenient to rewrite (2) and (3) in reduced forms in which T/T_m is replaced by τ and Pl by L. Thus

$$(4)\quad \left[\frac{d\tau}{dl} = P(1-\tau)\right]_{\tau \doteq 1}$$

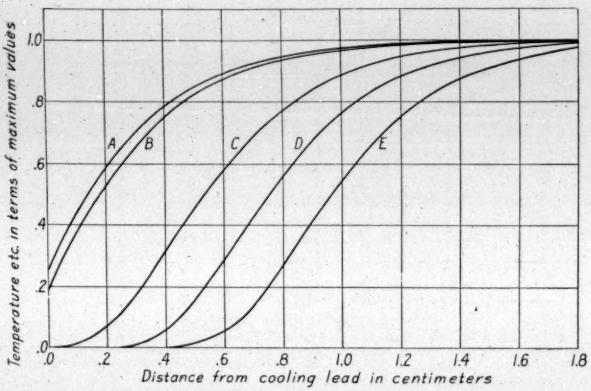
$$(5)\quad \left[1 - \tau = e^{-P(l-l')} = e^{-(L-L')}\right]_{\tau \doteq 1}$$

in which τ and L may be conveniently called reduced temperature and reduced length. Equation 5 gives the important generalization that *all end-loss curves in reduced units showing temperature variation with distance for a given substance are identical in the region where T approximates T_m,* that is, where τ approximates unity. The unit of τ is the central maximum temperature, the unit of L that distance along the filament where (5) applies, through which $1-\tau$ decreases to $1/e$ th of the value possessed at the beginning of the length interval. P is to be considered a transformation factor whereby lengths in ordinary units may be transformed into reduced units and *vice versa.* The ratio of two P's, when the end-loss curve giving the temperature variation corresponding to one of them is known, may evidently be used in accord with (4) to determine the temperature variation for the other in the region where T approximates T_m.

Distribution Curves for Long, Electrically-heated Tungsten Filaments in Vacuo.—The data used as a basis for computing

distribution curves for tungsten consist of a temperature scale,[8] the thermal conductivity,[8] the resistivity, and the radiation intensity functions[9] of temperature obtained by combining a determination of the brightness of a black body,[10] together with emissive powers and the deviation of the emission of tungsten from Lambert's cosine law[11] and results on thermionic emission.[12] The thermal conductivity data are the least satisfactory of all.

FIG. 1.



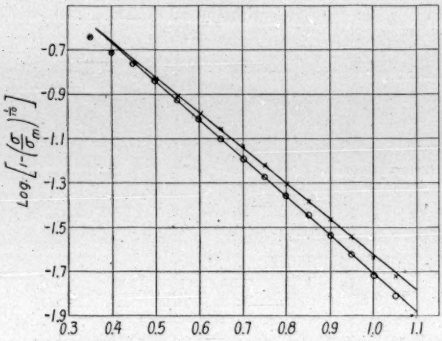
Various distribution curves for a long tungsten wire ($r = 0.01$ cm.) electrically heated in vacuo to a central maximum temperature of 2400° K. *A*, Temperature; *B*, Resistivity; *C*, Radiation intensity; *D*, Brightness; *E*, Thermionic emission intensity.

Curve *A*, Fig. 1, shows the temperature distribution for the particular case of a long tungsten filament having a diameter of 0.2 mm. electrically heated to a maximum temperature of 2400° K. The other distributions shown follow simply as stated from their known functions of temperature. Curve *C* was found to check exactly[4] with data published previously, giving σ as a function of l in a particular case.

It is a curious fact that, to a large extent, any one curve of Fig. 1 can be obtained by shifting any other curve laterally and without distortion by a fixed amount. Thus starting with the thermionic output curve *E*, successive shifts to the left of 0.22 cm., 0.43 cm., 0.78 cm., and 0.82 cm. give in succession the approximate positions of curves, *D*, *C*, *B*, and *A*.

The deviations of curve A, Fig. 1, from the form given by (3) in the region where T is considerably less than T_m, are not great. Moreover, a comparison of various computed curves corresponding to a considerable range of T_m showed these deviations to be always the same in direction and approximately the same in magnitude, and indicated that the generalization regard-

FIG. 2.



The radiation intensity distribution for a particular tungsten filament ($r = 0.01045$ cm.) heated to a maximum temperature of 2475° K. (1) by a current of 4.32 amps. directed away from the cooling junction (⊙⊙⊙), and (2) by a current of the same intensity directed toward the cooling junction (xxx).

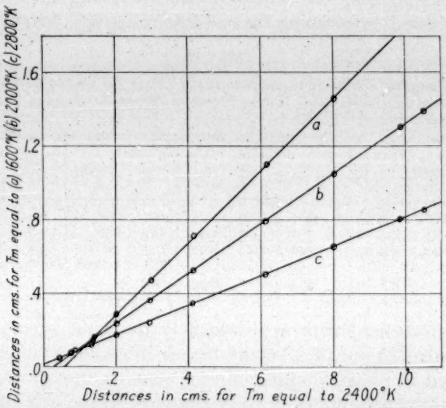
ing the identity of reduced distributions for the region where T approximates T_m might also apply outside this region in the case of tungsten. The broader application to include both regions requires further inquiry into its significance and its correctness. In a more specific way it states that, for any given value of τ $(=T/T_m)$, the temperature gradient dT/dl must vary as P. For test purpose, there are two independent phases corresponding to the two independent variables of which P is a function. One involves a variation in r, the other in T_m. Thus for filaments having different radii, but the same central operating temperature T_m, dT/dl must vary as $1/\sqrt{r}$, while for a given filament with various T_m values, dT/dl must vary as the corresponding Q's.

The first phase relating to varying radii is theoretically exact, and the experimental test generally verified the prediction, though with a considerable range of uncertainty which may well be

ascribed, among other things, to differences in filament manufacture and grain structure.

The second phase is theoretically inexact; but, due to being carried out wholly on a single filament, the test showed a much better verification. For a range of T_m values extending from 1976° K to 2667° K (the greatest range for which the writer has obtained distribution on a single filament in his past work),

FIG. 3.



Distances from a cooling lead in a long tungsten wire filament ($r = 0.01$cm.) heated electrically in vacuo to various central maximum temperatures T_m as a function of distances to corresponding temperatures when the maximum is 2400° K.

corresponding values of dT/dl were found to agree to within one or two per cent. This is based on a comparison of the slopes of the lines obtained when, as in Fig. 2, the empirical functions of radiation intensity $\log[1-\left(\frac{\sigma}{\sigma m}\right)^{1/10}]$ were platted against distances from the junction with the lead.

To see whether existing data are consistent with the varying T_m phase throughout a more extended range, computed distributions for such an extended range were compared. From additional curves similar to curve A of Fig. 1, corresponding to T_m values of 2800° K, 2000° K, and 1600° K, values of l corresponding to arbitrarily chosen values of T were platted against the l's for the same values of T from the 2400° K curve (see

Fig. 3). The points lie on straight lines whose slopes 0.80, 1.34, and 1.95 are quite closely given by the calculated ratios Q_0/Q (see Table II), namely 0.80, 1.32, and 1.91. Though the agreement is not exact, it is such as to indicate the substantial correctness of this phase.

As a close approximation, all end-loss temperature distribution curves for tungsten, platted in reduced units, are identical throughout.

Reasoning and tests similar to the foregoing show that similar conclusions concerning the end-loss resistivity, brightness, etc.,

TABLE II.

Data on Tungsten Useful in the Application of (2) to (6) and in the Determination of Unknown Distributions from a Standard Set on the Basis of Identical "reduced distribution" Curves.

T °K	σ watts/cm.	$\alpha = \frac{T}{\sigma}\frac{d\sigma}{dT}$	ρ ohm cm.	$\beta = \frac{T}{\rho}\frac{d\rho}{dT}$	k watts/cm. deg.	$\frac{T}{k}\frac{dk}{dT}$	b candles/cm.²	$\frac{T}{b}\frac{db}{dT}$	$\frac{T}{e}\frac{de}{dT}$	Q cm.$^{-½}$
2800°K	117.5	4.53	0.0₄887	1.20	1.27	0.4	688.	8.88	20.3	.470
2400	57.7	4.68	737	1.20	1.19	0.4	156.	10.3	23.6	.375
2000	24.2	4.87	592	1.20	1.11	0.4	20.0	12.3	28.2	.2835
1600	7.88	5.17	453	1.20	1.01	0.4	0.96	15.0	35.1	.1965
1200	.166	5.60	321	1.20	0.90	0.4	.....	.....	....	.116

distributions hold with approximately the same accuracy. The transformation factor whereby length in ordinary units may be expressed in reduced units and *vice versa* is in each instance P, as in the temperature case. For example, in the case of filament brightness, b, the equation analogous to (3), is

$$(6) \quad \left[1 - \frac{b}{b_m} = e^{-P(l-l')}\right] b = b_m.$$

The l' in this case differs from the l' of the temperature case by approximately the latteral shift which is necessary, as has been noted in discussing Fig. 1, to bring the two corresponding curves into practical coincidence.

Given curve A, Fig. 1, and the data of Table II, suppose the temperature distribution curve for a long tungsten filament 0.25 mm. in diameter with a maximum temperature of 2800° K is wanted. Representing by subscript 0 values referring to 2400° K, we have then for the transforming factor P/P_0, as shown by (4),

$$(7) \quad \frac{P}{P_0} = \frac{d\tau}{dl} \div \left(\frac{d\tau}{dl}\right)_0 = \frac{Q}{Q_0}\sqrt{\frac{r}{r}} = 1.122.$$

The 2800° K temperature distribution is therefore obtained by shortening all distance measurements on curve *A*, Fig. 1, by the factor 1.122. This distribution, it should be emphasized, is that obtained with an alternating current or the average of those

TABLE III.

Values of P/P_0 for Use in Conjunction with Equation 7 and Fig. 1 in Determining Distributions Corresponding to Various Filament Radii r and Central Maximum Temperatures T_m, and of P for Use in Conjunction with Equations 8 to 12 in Determining Effective Filament Shortenings, $\triangle l_A$, etc.

T_m in °K \ r in cm.		0.001	0.002	0.005	0.010	0.015	0.020	0.030
1000	P/P_0 =	.670	.472	.298	.211	.172	.149	.122
	P =	2.50	1.76	1.12	0.79	0.645	0.56	0.46
1200	P/P_0 =	.980	.690	.437	.309	.252	.218	.178
	P =	3.65	2.60	1.64	1.160	.945	.820	.670
1400	P/P_0 =	1.315	.930	.588	.416	.339	.294	.240
	P =	4.95	3.50	2.21	1.560	1.275	1.105	.900
1600	P/P_0 =	1.650	1.120	.740	.523	.427	.370	.302
	P =	6.20	4.38	2.77	1.965	1.605	1.390	1.135
1800	P/P_0 =	2.01	1.420	.898	.635	.518	.449	.366
	P =	7.55	5.32	3.36	2.38	1.940	1.680	1.375
2000	P/P_0 =	2.40	1.695	1.070	.758	.618	.536	.438
	P =	9.00	6.35	4.02	2.84	2.32	2.01	1.640
2200	P/P_0 =	2.777	1.955	1.235	.875	.714	.618	.505
	P =	11.35	7.35	4.64	3.28	2.68	2.32	1.895
2400	P/P_0 =	3.16	2.24	1.415	1.000	.816	.707	.578
	P =	11.85	8.40	5.30	3.75	3.06	2.65	2.16
2600	P/P_0 =	3.56	2.52	1.590	1.125	.918	.796	.650
	P =	13.35	9.45	5.96	4.22	3.45	2.98	2.44
2800	P/P_0 =	3.96	2.80	1.775	1.254	1.024	.887	.724
	P =	14.85	10.50	6.65	4.70	3.84	3.32	2.71
3000	P/P_0 =	4.38	3.10	1.960	1.385	1.130	.980	.800
	P =	16.40	11.60	7.35	5.19	4.23	3.67	3.00

obtained at the two ends of a filament heated by a direct current. For the convenience of others, a group of values for P/P_0 are given in Table III.

Granted the foregoing conclusions, the development of general expressions for integral end-losses is much simplified. Without question, for end-loss correction purposes, errors made by assum-

ing the identity of the reduced distributions are less than other experimental uncertainties.

End-loss Corrections.—An end-loss may be most satisfactorily viewed as an effective filament shortening. Referring to Fig. 1, curve *D*, it is easily seen that, from a light production standpoint, the filament is effectively about 0.8 cm. shorter than it would be were the filament uniformly bright all the way to the lead. The effective length of the filament is thus shortened by about 0.8 cm. Similarly, from the thermionic emission standpoint, the effective filament shortening is about 1.0 cm., etc. The exact shortening in any case will depend on the temperature T_j at the junction of filament to the lead or support.

For most purposes only rough estimates of T_j are necessary. In illustration, compare the temperature distribution of Fig. 1 in which T_j equals 600° K with that for the same filament operated at the same T_m but with T_j equal to 800° K. Evidently the part of the filament between 600° K and 800° K for the first case bears the same relation to the portion beyond the 800° K point that the junction in the second case bears to the filament as a whole; and hence, beyond the 800° K points, the distributions are identical. Referring to Fig. 1, it will be seen that the two cases differ in effective shortenings by about 0.04 cm. Unless otherwise stated, in this paper T_j is assumed to be $T_m/4$.

On the basis of identical reduced distributions, each of the effective shortenings varies as $1/P$. Representing by Δl_A, Δl_B etc., in accord with the lettering of the curves of Fig. 1, the effective filament shortenings at a single junction from the standpoint of heat content, resistivity or energy input, radiation output, light emission, and thermionic emission; and evaluating proportionality constants from the plat, we obtain the following simple end-loss expressions, giving values in cm.

$$(8)\quad \Delta l_A = 0.88\sqrt{r/Q} = 0.88\, 1/P \quad \text{(heat content)}$$

$$(9)\quad \Delta l_B = 1.00\sqrt{r/Q} = 1.00\, 1/P \quad \text{(energy input)}$$

$$(10)\quad \Delta l_C = 2.25\sqrt{r/Q} = 2.25\, 1/P \quad \text{(radiation output)}$$

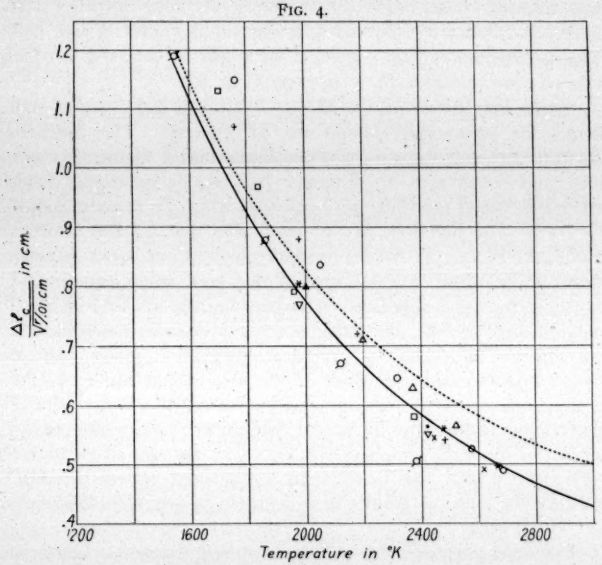
$$(11)\quad \Delta l_D = 3.00\sqrt{r/Q} = 3.00\, 1/P \quad \text{(light emission)}$$

$$(12)\quad \Delta l_E = 3.85\sqrt{r/Q} = 3.85\, 1/P \quad \text{(thermionic emission)}$$

To apply these equations it is necessary to know r and T_m. Once T_m or r is known; the others may be determined from wattage and resistance considerations.[9]

Equations 8 to 12 indicate that, other things unchanged, the effective filament shortenings vary as $\sqrt{r}$. The variation in total filament length with radius for vacuum lamps operating at the same voltage and temperature follows the same law. Hence, other things unchanged, the percentage end-losses for lamps of

FIG. 4.



Observed effective filament shortenings due to a single cooling junction from the radiation output standpoint $\triangle l_c$, for various sized tungsten filaments (.00025 cm. $< r <$ 0.013 cm.) reduced to give expected shortenings for a filament having a radius of 0.01 cm., platted as a function of the maximum temperature, T_m. The full line represents calculated values for the case $T_j = \frac{T_m}{4}$, the dashed line values for the case $T_j = 300°$ K.

different wattage but the same voltage and the same temperature of operation are the same. The percentage end-loss in a 10-watt, 115-volt lamp, is the same as that in a 100-watt, 115-volt lamp.

A test of any one of equations 8 to 12 is a test of all, since all of the physical properties are definite functions of the same independent variable, T. Selecting 10 as convenient, data previously obtained have been gone over and wherever possible determinations of Δl_C computed. In Fig. 4, these have been

platted as functions of T_m. The full line represents equation 10. Considering possible variations in T_j due to difference in lamp construction, in crystal structure resulting from changes in lamp manufacture and from differential temperature treatment in any single filament during previous operation, and in filament diameter resulting from vaporization during previous operation, the agreement between observed and computed values is not bad. The dashed line of Fig. 4 gives what might be expected if equation 10 were corrected for a common T_j or 300° K.

Some indications of the energy input and light output end-losses for commercial lamps are of interest. The ordinary 40-watt, 115-volt vacuum tungsten lamp with a filament 51 cm. long and 0.038 mm. in diameter has two large copper leads and eleven small molybdenum hook supports. T_m is about 2450° K. The lead junctions are of such size that T_j lies between $T_m/4$ and $T_m/3$. T_j for the smaller molybdenum hooks is much larger about 1750° K. Because of this high value, equations 8 to 12 are not applicable here. However, on the basis of identical reduced distributions, the end-loss for any described condition is not difficult to obtain by graphical integration using Fig. 1. Doing this and taking account of the fact that at the hooks the cooling extends both forward and backward, the total effective shortenings in the lamp have been determined. From the energy input and the light output standpoints they amount to about 1.1 cms. and 5.2 cms., that is, to about 2.2 per cent. and 10 per cent. Whence the end-loss results in a decrease in luminous efficiency of 7.8 per cent.

For most purposes, the end-losses in long filaments, whatever the values of r and T_m, may be computed with considerable precision with the aid of equations 8 to 12.

THE SHORT FILAMENT.

The short filament for this purpose is defined as one in which the cooling effects due to the leads or supports appreciably affect the temperature of the central portion. In contrast to the long filament, the total cooling effect at some points at least are due to two separate leads or supports.

In the long filament in vacuo near the centre of its length, the rate of production of heat in any element of length is equal to the rate of radiation of energy from its surface. In the short

filament this equality does not hold; there is always a net rate of transfer of heat by conduction out from the ends of the element of length toward one of the leads or supports. It is this characteristic difference which results in the differences in the end-loss curves for the two kinds of filaments.

Equation 1, with conditions characteristic of short filaments, introduced leads to an expression which shows well the similarity and the difference which short filament distributions bear to long filament distributions. It is

$$(13)\quad \left(\frac{dT}{dl}\right)^2_{\substack{T\\ \text{short}}} = \left(\frac{dT}{dl}\right)^2_{\substack{T\\ \text{long}}} - \left(\frac{dT}{dl}\right)^2_{\substack{T_\mu\\ \text{long}}}$$

in which by the double subscript the temperature and the type of filament are specified. In illustration, consider two filaments of the same cross-section, one long and the other short, which are heated by the same current to central maximum temperatures $T_m = 2400°$ K and $T_\mu = 2000°$ K, respectively. Then $\left(\frac{dT}{dl}\right)^2$ for the short filament at the point where $T = 1800°$ K, say, is equal to $\left(\frac{dT}{dl}\right)^2$ for the long filament at 1800° K less $\left(\frac{dT}{dl}\right)^2$ for the long filament at 2000° K. In a plat of $\left(\frac{dT}{dl}\right)^2 = f(T)$ the curve for the short filament is obtained by shifting the curve for the long filament perpendicular to the T axis until it intersects at 2000° K. This condition greatly simplifies the treatment of short filaments, which also may be shown to follow the reduced distribution principle. Any desired distribution may be obtained from a standard set.

A standard set of distribution curves for various short tungsten filaments 0.2 mm. in diameter, together with the method for using them and the results of tests, will be published in a fuller discussion elsewhere.

THE RIBBON FILAMENT.

Assuming identical properties for the filament materials, it follows that end-losses for ribbon filaments are related simply to those for cylindrical or wire filaments. The fundamental end-loss equation differs from (1) by the substitution of the expressions for the cross-sectional area wt and the perimeter $2(w + t)$

of the ribbon for the analogous wire expressions πr^2 and $2\pi r$. Further equations and theory are modified only by the substitution of $(1/w + 1/t)$ for $1/r$, *e.g.*,

$$(14) \quad P = Q\left(\frac{1}{w} + \frac{1}{t}\right).$$

The reduced distribution curves for ribbon are identical with those for wire filaments, both long and short. The effective shortenings are identical when for the same T_m or $T\mu$ $(1/w + 1/t)$ equals $1/r$.

In equivalent wire and ribbon filaments (that is in filaments having the same resistance and the same wattage for the same T_m) operated at the same T_m, the percentage end-losses are equal.

The above conclusions were tested in a comparison of a wire filament 3 cm. long and about 0.12 mm. in diameter with a ribbon filament 2 cm. long and an approximate cross-section of .029 mm. $\times$ .25 mm. Allowing for the small deviation from equivalence, the two lamps were found, when operated at the same temperatures, to have the same luminous efficiency to well within the uncertainties of measurements, though the reductions due to the ends were of the order of 30 per cent.

Reasoning similar to the above shows that, whatever the cross-section of the filament, the end-loss expressions may be obtained by substituting the ratio of its cross-section to its perimeter for $r/2$ in the corresponding expressions for wire filament.

SUMMARY.

The Long Filament.—General expressions for the temperature, resistivity, emission intensity, brightness, and thermionic emission distributions near a cooling junction, for uniform electrically heated filaments mounted in vacuo, have been derived. Those computed for tungsten were found to check observed distributions closely. It was found that, for each type of distribution curves, there is a single reduced distribution from which by means of a simple theoretical transformation factor P (see Table I) any desired distribution may be obtained with considerable exactness. It follows that the various effective filament shortenings from different standpoints, *i.e.*, the effective measures of end-losses, vary inversely as the transformation factor P (equations 8 to 12).

The Short Filament.—The relation of the distribution curves for short filaments to those for long filaments is shown, and it is pointed out that there is a family of reduced distribution curves from which any one desired curve may be obtained.

The Ribbon Filament.—Equations and conclusions developed for cylindrical or wire filaments apply equally well to filaments with rectangular and other cross-sections when the ratio of twice the cross-section to the perimeter of the filament is substituted for the radius of the cylindrical filament. For equivalent filaments (equal resistances and wattages at the same operating temperatures) operated at the same temperature, the percentage end-losses are the same.

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[3] WORTHING, *Phys. Rev.*, **4**, p. 524, 1914.
[4] WORTHING, *Phys. Rev.*, **4**, see footnote, p. 538.
[5] WORTHING, *Phys. Rev.*, **5**, p. 445, 1915.
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[10] HYDE, FORSYTHE and CADY, *Phys. Rev.*, **13**, p. 45, 1919.
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Preparation of Perchlorates by Heating Chlorates.—MATHERS and JONES, respectively of the Indiana State University and the Research Department of the Roessler and Hassler Chemical Company, St. Alban's, Vermont, have investigated the comparative yields of the electrolytic and direct heating processes for obtaining perchlorates. They failed to find any method by which the yield in the heating process can be increased over that heretofore obtained. Additions of different substances were made in hopes of establishing a catalytic effect, but none served the purpose, and most decreased the yield. The maximum yield was obtained by heating from 1 to 50 grams of potassium chlorate at from 480 to 560° C. for from 30 to 60 minutes. The yield was about 55 per cent. Sodium chlorate gave lower results, and several other chlorates were largely decomposed to chloride. The use of perchloric acid for electrolytic purposes makes its production important. H. L.

Lectures Before Local Sections of the American Chemical Society.—Arrangements have been made through the American Chemical Society for lectures to be delivered before the local sections by Professor E. C. Franklin of Leland Stanford University on dates during the latter part of March and early part of April. Several sections have already fixed dates. Applications for lectures should be made to E. M. Billings, Kodak Park, Rochester, New York. H. L.

The Luminescence of Incandescent Solids. E. L. NICHOLS and H. L. HOWES. (*Phys. Rev.*, April, 1922).—Any incandescent solid emits light because of its high temperature. Here we learn that there are solids that in a state of incandescense emit light not due to their temperature. The presence of luminescence is esablished whenever it can be shown that the body emits more intense light of any wavelength than is emitted at the same temperature by a black body, the best radiator by reason of temperature alone. At 665° C. CaO emits only .00432 as intense red light as a black body sends out. This fraction becomes three times as great at 735° C., twenty-six times as great at 837° and passes through two maxima before 1606° is reached, but at no temperature does it equal unity. There is thus no luminescence in respect to red. With blue it is quite a different story. The ratios which above were proper fractions are for blue light the following whole numbers for the four temperatures named—216, 52, 14, and .232. The result is so surprising that it merits setting forth in bold relief. Calcium oxide at a temperature at which it is barely luminous emits blue light 216 times as intense as that emitted by a black body at the same temperature. At the same temperature the corresponding ratio is for Al_2O_3, 400; SiO_2, 195; ZrO_2, 53; NbO, 2150. For NbO at 560° C. the ratio is 85,200, an astounding outcome. Luminescence in the red as well as in the blue was found in the cases of the oxides of praesodymium, neodymium, erbium, cerium, gallium, niobium, samarium, gadolinium, aluminium, zirconium, silicon and beryllium, and several points of maximum value are common.

The heating of the oxide under observation was done by the use of an oxy-hydrogen flame with a small content of oxygen. The use of this heating agent was determined by the fact "that the effect we were seeking is only indirectly related to temperature but is greatly stimulated and enhanced by the conditions existing in the oxy-hydrogen flame."

When an oxide was heated for the first time the intensity of the light emitted was greatest at first and diminished with time. For magnesium oxide the ratio was 65 at an instant .3 sec. after ignition. After several minutes it became less than one.

The authors connect the phenomenon they describe with changes in the physical state of the oxides, such as the electrical resistance. "It is as though during such rearrangements in the structure, the light-producing process which we term luminescence can go on."

G. F. S.

THE SAMPLING AND ANALYSIS OF AUTOMOBILE EXHAUST GAS.*

BY

A. C. FIELDNER AND G. W. JONES.

U. S. Bureau of Mines.

INTRODUCTION.

ANALYSES of samples of exhaust gas taken during road tests of 101 automobiles and trucks [1] under normal conditions showed an astonishing loss of gasoline due to incomplete combustion, and at least half of this loss could have been prevented by proper adjustment of their carburetors. A simple determination of the percentage of carbon dioxide in the exhaust gas affords a ready and scientific means of determining the completeness of combustion, and of adjusting the carburetor to give maximum efficiency. Part or complete gas analyses are valuable to the automotive engineer in solving problems in vaporization, manifold condensation, distribution to the cylinders, and combustion in the cylinders. The total volume of exhaust gases, the air-gasoline ratio, and the percentage of completeness of combustion may be calculated from the gas and gasoline analyses, and the quantity of gasoline used. It may be of some value, therefore, to the automotive and petroleum industries, to describe the methods of sampling and analyzing exhaust gases which were developed and used by the Bureau of Mines in connection with investigations pertaining to the ventilation of vehicular tunnels [2] and fuel economy in internal combustion engines.[3]

* Communicated by the Director of the Bureau of Mines.

[1] Fieldner, A. C., Straub, A. A., and Jones, G. W., Bureau of Mine Reports of Investigations, Serial No. 2225, March, 1921.

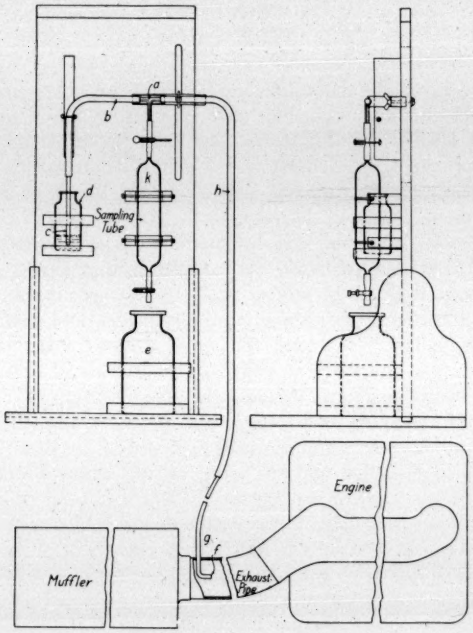
[2] Fieldner, A. C., Appendix No. 3—Tunnel Gases Investigations—Amount and Composition of Automobile Exhaust Gases; pages 91 to 140, Report of the New York State Bridge and Tunnel Commission 1921, Legislative Document No. 64 (1921).

[3] Fieldner, A. C., Straub, A. A., and Jones, G. W., "Gasoline Losses Due to Incomplete Combustion in Motor Vehicles," *Jour. Ind. Eng. Chem.*, vol. 13, 1921, pp. 51; *Jour. Soc. Automotive Engineers*, vol. 8, p. 295; Bureau of Mines Reports of Investigation, Serial No. 2225, March, 1921.

METHODS OF SAMPLING EXHAUST GASES IN ROAD TESTS.

A convenient apparatus for taking exhaust gas samples is shown in Fig. 1. The sampling tube *g*, of 1/4, 5/16, or 3/8-inch copper tubing, depending upon the size of car or truck, is introduced in the exhaust manifold between the engine and the muffler,

FIG. 1.

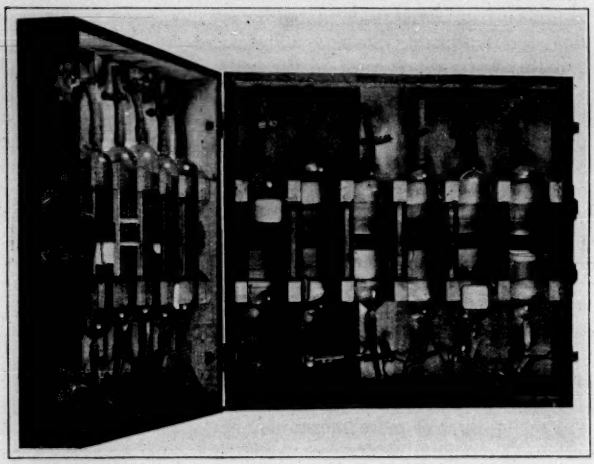


Attachment for taking samples of exhaust gas.

with the opening *f* turned directly against the flow of gases. A gas-tight fit is obtained by using a clamp in two halves made to fit snugly around the exhaust pipe, and held in place by four bolts passing through both sections of the clamp. The copper tube is brazed into the upper half of the clamp, and is made gas-tight where it passes through the exhaust pipe by a layer of asbestos and graphite packing. The copper tube is extended

back along the exhaust pipe (to prevent freezing of moisture in cold weather), and up through the floor of the car where connection is made to a ¼-inch heavy-walled rubber tube *h*, which is connected to the glass tee *a*. The main stream of exhaust gases passes on through the rubber tube *b*, and is discharged into the atmosphere through the water-seal *c*, in the bottle *d*, thus preventing any air from being sucked back into the sample. A rapid stream of gas should flow out at the water-seal when the

FIG. 2.



Carrying cases for sampling tubes.

engine is running. The gas sample containers, or sampling tubes *k*, are of 250 c.c. capacity, and are made of glass tubing about 1½ inches in diameter, drawn out and sealed to capillary tubes to fit a 3/16-inch rubber tube at each end. The rubber connections are carefully wired gas-tight. Heavy-walled composition rubber tubing is best adapted for use with the screw-clamp which regulates the rate of discharge of the water from the lower end of the container, and 3/16-inch pure gum rubber tubing gives a gas-tight seal with a strong spring clamp at the upper end of the container.

The sample containers are completely filled in the laboratory with water containing 5 per cent. sodium chloride, and are saturated with exhaust gases to reduce the solubility of carbon dioxide, and are transported in wooden carrying cases, as shown in Fig. 2. The water-filled container is attached to the tee *a* (Fig. 1) by slipping the pure gum tubing moistened with water over the lower branch of the tee, and is held in place on the board by two rubber bands as shown. The gas sample is then taken continuously over the whole period of a given test, by opening the upper pinch-clamp and the screw-clamp on the lower end of the container, and adjusting it to allow the container to become empty at the exact time for terminating the test. The water flows into the jar *e*, and this water is returned to the laboratory for refilling other sample containers. One observer should give his entire attention to taking the gas samples and regulating the flow of water from the gas-sample container by readjusting the screw-clamp at regular intervals, so that all the water is displaced by gas at the end of the test. No water should remain in contact with the gas other than which adheres to the walls and the few drops that remain in the capillary ends of the container.

ACCURACY OF SAMPLING METHODS.

The securing of a gas sample which represents the average composition of the entire quantity of exhaust gas produced during a given test with a fair degree of accuracy is of fundamental importance in determining the quantity of each constituent produced. Two methods of procedure may be considered, namely, (1) taking three or more intermittent or "grab" samples in each test and averaging the analyses; and (2) taking a single continuous sample of exhaust gas at a uniform rate during the entire period of each test.

GRAB OR INTERMITTENT METHOD OF SAMPLING.

In this method the sample container of glass or metal, fitted with stopcocks at each end, is attached to a short metal tube ¼ inch in diameter, which is inserted in the exhaust-gas manifold between the muffler and engine, as shown in Fig. 25, of Bureau of Mines Bulletin 74.[4] The exhaust gas is allowed to flow through the container for a sufficient length of time to ensure

[4] Hood, O. P., Kudlich, R. H., and Burrell, G. A., "Gasoline Mine Locomotives in Relation to Safety and Health," Bull. 74, Bureau of Mines, 1915, 84 pp.

complete purging of the air. Both stopcocks are then closed, and the container is removed for analysis of the contents.

Advantages of Grab Method.—(a) No confining liquid is necessary, and errors of solution of exhaust gases in this liquid are eliminated.

(b) It is simple and convenient to carry out during road tests.

Disadvantages of Grab Method.—(a) It represents only a small fraction of the test, therefore three or more samples would be required in each test to give a representative average analysis. Road tests of automobiles are subject to fluctuating power demands and constant changes of throttle position, so the analysis of each of these many samples would entail much more work than would be connected with taking a representative average sample which would include all variations during the entire test.

(b) There is danger of the exhaust gas not completely displacing the air in the containers.

CONTINUOUS METHOD OF SAMPLING.

A properly taken continuous, or rather proportional, sample should be of exactly the same composition as the entire exhaust gas given off during a test. While it cannot be taken in an exact proportion to the quantity of gas given off at each moment, it can be taken at a uniform rate throughout the test by regulating the flow of a fluid from the container; and if the test course and speed is fairly uniform, the sample should also be approximately proportional, at least more so than a small number of grab samples.

POSSIBILITY OF ERRORS.

Although mercury is the ideal fluid for use in continuous gas sampling because none of the gases dissolve in it, the large number of samples that may be taken each day while on the road makes the use of mercury practically out of the question. The use of water was therefore investigated with especial reference to the magnitude of possible errors resulting from solution of carbon dioxide, as this is the only constituent of exhaust gases that is materially soluble in water. In order to reduce the opportunity of solution, a narrow tubular gas sample container was used, so that only a comparatively small surface area of water was in contact with the gas. The solubility of carbon dioxide in water varies with the temperature; at ordinary room tempera-

ture, 1 c.c. of distilled water will absorb approximately 1.0 c.c. of carbon dioxide, if the gas above the liquid is 100 per cent. carbon dioxide. As the percentage of carbon dioxide decreases the amount absorbed diminishes; 14.6 per cent. carbon dioxide is the maximum possible quantity in exhaust gases with complete combustion of gasoline containing 85 per cent. carbon.

Error Due to Absorption of Carbon Dioxide.—The following series of tests were made in which air containing various known quantities of carbon dioxide was sampled simultaneously in two parallel sampling outfits similar to those used in the automobile tests. Mercury was used in one container and water in the other.

1. Carbon dioxide absorbed in tap water under sampling conditions, from a 15 per cent. CO_2-air mixture:

Experiment No.	Carbon dioxide, per cent. By mercury.	Carbon dioxide, per cent. By water.	Difference.	Time to collect sample in minutes.
1	15.2	14.2	1.0	20
2	15.0	14.2	0.8	10
3	14.9	14.0	0.9	5

2. Carbon dioxide absorbed in water previously saturated with air containing 20 per cent. of CO_2, under sampling conditions, from a 19 to 20 per cent. CO_2-air mixture:

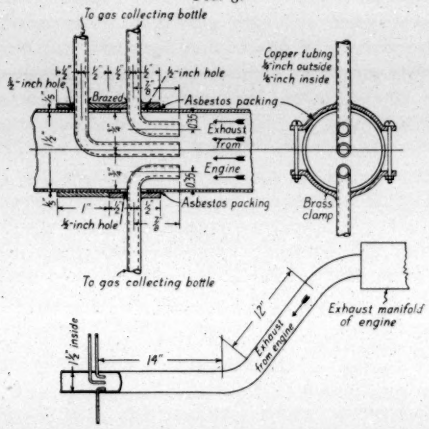
Experiment No.	Carbon dioxide, per cent. By mercury.	Carbon dioxide, per cent. By water saturated with 20 per cent. CO_2 in air.	Difference.	Time to collect sample in minutes.
1	19.5	19.1	0.4	20
2	18.6	18.4	0.2	20
3	19.5	19.1	0.4	10
4	18.6	18.6	0.0	10
5	18.6	18.6	0.0	5

3. Carbon dioxide absorbed or given off from the same water solution used in gas containers of previous experiment, under sampling conditions, from a 12 per cent. CO_2-air mixture:

Experiment No.	Carbon dioxide, per cent. By mercury.	Carbon dioxide, per cent. By water from previous experiments.	Difference.	Time to collect sample in minutes.
1	11.8	12.1	0.3	20
2	11.8	11.8	0.0	10
3	11.8	11.6	0.2	5

These experiments show a maximum error of 1 per cent. in the carbon dioxide content when using tap water over a sampling period of 5 to 20 minutes. Water saturated with a 20 per cent. CO_2-air mixture, and used in sampling air containing 20 per cent. CO_2, and subsequently in sampling air containing 12 per cent. of CO_2, showed differences or errors not exceeding 0.2 to 0.3 per cent. Therefore, it is safe to assume that the error due to absorption of CO_2 will never exceed 0.5 per cent. of the sample

FIG. 3.



Sketch of position of sample tube to check gas composition at various points.

analyzed if the water is first saturated with air containing 10 to 12 per cent. of carbon dioxide, and then this same water is used repeatedly. In the Bureau of Mines road tests, 5 per cent. of sodium chloride was dissolved in the water to lower further the solubility of carbon dioxide, also to lower the freezing temperature of the water, as many of the tests were made in extremely cold weather.

Errors Due to Position of Sampling Tube in Exhaust Pipe.—In order to determine the composition of the exhaust gases at different points in the cross-section of the exhaust pipe, and to ascertain how closely a sample tube placed in the centre represented the average composition, a series of tests were conducted with sample tubes in different positions as follows:

Three sample tubes were fixed in a transverse plane of the exhaust pipe, respectively at ¼, ½, and ¾ of the inside diameter of the pipe. In conducting these tests, the motor was allowed to run sufficient time to become thoroughly warmed. Gas sample collecting tubes were then attached to each of the sampling tubes. (See Fig. 3.) The three samples were drawn at the same uniform rate for the period of the test. Tests were made on two different dates with the car standing, engine racing and engine idling. On each test and on each date, duplicate exhaust gas samples were taken for each condition of operation, during which time neither the position of the spark nor throttle was changed. The tests were each of four minutes' duration, and the percentage of CO_2 in the gas samples collected are shown by Table I, following:

TABLE I.

Results of Tests on Position of Sampling Tube in Exhaust Pipe Tests, Showing Variation of CO_2 Percentage in Samples Taken from Different Pionts.

Test No.	Test condition.	CO_2 in exhaust, per cent.			Average CO_2 per cent.	Variation of average from centre sample, per cent.
		Top.	Centre.	Bottom.		
1 – A	Standing, engine racing	9.8	9.7	8.3	9.3	— 0.4
1 – B	Standing, engine racing	9.0	9.3	9.0	9.1	— 0.2
2 – A	Standing, engine idling	6.7	6.8	6.5	6.7	— 0.1
2 – B	Standing, engine idling	6.0	6.6	6.2	6.3	— 0.3
3 – A	Standing, engine racing	9.6	9.4	9.4	9.5	+ 0.1
3 – B	Standing, engine racing	9.9	9.6	9.8	9.8	+ 0.2
4 – A	Standing, engine idling	6.5	6.3	5.8	6.2	— 0.1
4 – B	Standing, engine idling	6.3	6.3	5.1	5.9	— 0.4
	Average	8.0	8.0	7.5	—	0.2

The tests indicated as A and B are repeat tests made on the same day under the same conditions. The maximum variation of the percentage of CO_2 in the exhaust sample taken from the

centre position when compared with the top, middle, and bottom was found to be 0.4 per cent., and the average of the average variation is 0.2 per cent. It will be noted that repeat tests under the same conditions may vary by 0.4 per cent., therefore the sampling of the exhaust from the centre is justified, and is within the experimental error of making duplicate tests under the same condition.

Further justification of placing the sampling tube in the centre of the exhaust pipe is shown by results obtained during tests made to check the quantity of exhaust gas liberated by an engine first as calculated from the gasoline used and the exhaust gas analysis, and secondly, by actually measuring the gases by running them into a 50-cubic foot tank from which water was run out as fast as the gases were introduced. During these tests, a continuous sample of the gas was taken from the centre of the exhaust pipe, and then after the gas in the tank was measured, a sample was taken from the top, middle, and bottom of the tank. The amount of CO_2 in these samples is shown in Table II. The maximum variation of the three tank samples, compared with the continuous sample taken from the centre of the exhaust pipe, show a remarkably close agreement, the maximum CO_2 per cent. variation being only .1 per cent.

TABLE II.

Results of Tests Showing Accuracy of Method of Sampling Exhaust Gas from Centre of Exhaust Pipe, as Compared with Sampling Total Exhaust Liberated. (Only the CO_2 percentages are given to show variation of composition of exhaust gas taken from centre of exhaust pipe and in tank.)

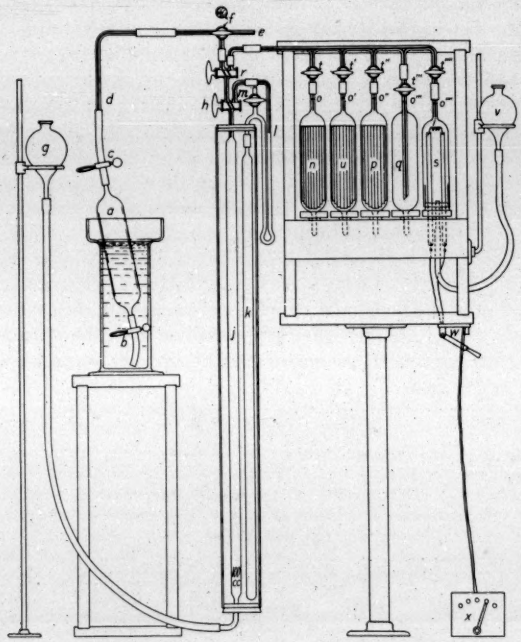
Test No.	CO_2 in exhaust gas in tank, per cent.			Average CO_2 per cent.	CO_2 in continuous sample from middle of exhaust pipe, per cent.	CO_2 variation per cent.
	Top.	Middle.	Bottom.			
1	7.6	7.7	7.8	7.7	7.7	0.0
2	5.6	5.9	5.8	5.8	5.7	0.1
3	5.7	6.1	6.0	5.9	6.0	0.1

COMPLETE ANALYSIS OF EXHAUST GAS.

Apparatus.—Complete analysis of exhaust gas includes the determination of CO_2, O_2, CO, H_2, CH_4, C_2H_4, and N_2 (by difference). The CH_4 determination is not strictly all methane, but is

really the methane equivalent of the hydrocarbons in the gas. The special modified type of Orsat apparatus, shown in Fig. 4, is best adapted for speed and accuracy in analyzing exhaust gases. It consists essentially of a 100 c.c. water-jacketed burette *j*, compensating tube *k*, four absorption pipettes *n*, *u*, *p*, and *q*;

FIG. 4.



Laboratory apparatus for complete analysis of automobile exhaust gases.

and slow combustion pipette *s*. Mercury is used as the confining fluid in the burette and combustion pipette, and for displacing the sample in the container *a*.

The burette is graduated in 1/10 c.c., every fifth mark extending half-way around the burette. The even cubic centimetres are etched on the burette, and the 100-c.c. mark is placed at the

bottom. The tubes *n*, *u*, and *p* are simple absorption pipettes filled with the proper reagents and glass tubes to give better contact between the gas and absorbent; *n* contains potassium hydroxide solution for absorbing carbon dioxide, *u* contains fuming sulphuric acid for absorbing unsaturated hydrocarbons, and *p* contains potassium pyrogallate solution for absorbing oxygen. The tube *q* is a bubbling pipette, and contains acid cuprous chloride solution for absorbing carbon monoxide. Enough reagent is placed in each pipette so that when they are drawn to the marks *o*, *o'*, *o''*, and *o'''*, sufficient reagent remains in the rear branch of the pipette to form an adequate seal. Rubber bags should be attached to the rear branches of each pipette to prevent access of air to the reagents.

The combustible gases, consisting of methane (hydrocarbons), hydrogen, and carbon monoxide, not absorbed by the cuprous chloride, are burned by slow combustion in the pipette *s*, which contains a platinum coil *i* of No. 30 B. & S. gage wire 2¼ inches long. The ends of the coil are inserted in the tops of two glass tubes extending out through the rubber stopper in the bottom of the pipette. Stout loops of platinum wire are sealed into the bottom of these tubes. For 110-volt a. c. current, these loops are connected to the secondary of a 150-watt toy transformer having a variable voltage ranging from 1½ to 30 volts. A piece of No. 32 B. & S. gage nichrome wire 16 inches long is stretched between two binding posts mounted on the bottom board of the wood frame above the switch *w* (not shown in the figure). The binding post on one end of this wire and a sliding contact on it are connected into the circuit to permit close adjustment of the temperature of the platinum coil. The glass tubes in the combustion pipette are filled with mercury to complete the electrical circuit before inserting them in the pipette. After the pipette is mounted in place, mercury is poured into the bulb *v* until the level *o''''* is reached.

Leveling bulbs *g* and *v* are supported by iron stands and adjustable ring supports as shown in the figure.

A good Orsat apparatus calls for the highest grade of workmanship in construction and assembling of the parts. The capillary train should be of 1½ to 2 mm. inside bore and of 7 mm. external diameter, so that tight connections may be maintained

throughout. It should all be made of the same kind of glass, and must be well annealed. Above all, the stopcocks must have liberal bearing surfaces and must be accurately ground. The stopcocks should be lubricated with a special stopcock grease consisting of 50 parts by weight of pure gum rubber, 10 parts of vaseline, and 25 parts of beeswax.

Operating Procedure (*Testing Tightness of Apparatus*).—Draw into the burette about 50 c.c. of air, then turn cocks *h* and *r* to communicate with the train of pipettes. Raise the levelling bulb *g* so as to place the confined gas under a pressure of about eight inches of mercury. Any leaks in the stopcocks or rubber connections are shown by the mercury slowly rising in the burette. This procedure, however, does not indicate any leaks in the rubber connections below stopcocks *t*, *t'*, *t''*, etc. Any leaks at these connections are shown by the solutions falling from the marks *o*, *o'*, *o''*, and *o'''*, after standing for a time.

Measuring the Sample.—Before beginning a series of analyses, see that the compensator tube *k* and the burette contain enough water to ensure saturated gases, and that the compensator U-tube *l* is filled with mercury to mark *l*. Sweep the capillary train free from oxygen by drawing a sample of air into the burette and passing it into the "pyro" pipette *p* until all the oxygen is removed. Then pass this nitrogen through all the other pipettes to remove oxygen. In succeeding determinations this preliminary removal of oxygen is unnecessary, as nitrogen only remains in the apparatus after an analysis. Adjust the gas in the compensator tube to atmospheric pressure by momentarily removing the three-way cock *h* and compensator cock *m*. Adjust all the reagents in the absorption pipettes and the mercury in the combustion pipette to the marks *o* on the capillaries.

Turn stopcocks *h*, *r*, and *f* to communicate with the outside air at *e*, slowly raising levelling bulb *g* until the mercury reaches *f*. Connect the exhaust gas sample tube with *d*, and dip the lower end into the mercury container. Squeeze out all air bubbles from the rubber connection, then open the clamp *b;* turn stopcock *f* to communicate with the sample, lower levelling bulb *g* slightly, and open clamp *c* at top of sample tube, allowing about 30 c.c. of gas to enter the burette. Reject this sample through cock *f* and the free end *e*, as it is contaminated with air from the connec-

tions. When the mercury reaches *f*, turn the cock to communicate with the sample, and draw about 50 c.c. of sample into the burette as previously directed. Close pinch-clamp *c*, turn *r* through 180 degrees connecting to the absorption train, and then turn *f* to the air.

Now turn *h* through 180 degrees, thus connecting the burette and compensator, and raise or lower bulb *g* until the mercury in the compensator U-tube reaches the mark *l*. Read and record the volume of sample taken to the nearest 0.05 c.c.

Carbon Dioxide.—Turn *h* through 180 degrees, and raise levelling bulb *g* slightly to put the sample under pressure, thus avoiding any possibility of pulling the caustic solution into the cock *t;* then turn cock *t* to admit the sample from the burette to the caustic pipette, continue raising *g* slowly until the mercury reaches *h;* lower the levelling bulb slowly, drawing the gas back into the burette until the caustic solution covers the glass tubes in the pipette; again pass into the caustic pipette, and return it to the burette, repeating this operation until all of the CO_2 is absorbed. Finally, bring the level of the reagent to the mark *o* very carefully to avoid getting any solution into the stopcock *t;* close stopcocks *t*, turn *h* to communicate with the compensator, and adjust the mercury level in the compensator manometer to the mark *l*. Read and record the volume of gas. Repeat the above operations until no further contraction in volume takes place. If more than 10 passes are required to get complete absorption, the caustic solution should be replaced with a fresh one. The final burette reading subtracted from the original volume is the contraction due to the absorption of carbon dioxide.

$$\text{Percentage of } CO_2 = \frac{\text{Contraction} \times 100}{\text{c.c. of sample taken.}}$$

Unsaturated Hydrocarbons.—Pass the gas six times into the fuming sulphuric acid pipette, then remove the SO_3 vapors by passing the gas into the caustic pipette *n*, and return it to the burette for reading the contraction as prescribed under the determination of carbon dioxide.

$$\text{Percentage of unsaturated hydrocarbons} = \frac{\text{Contraction} \times 100}{\text{c.c. of sample taken.}}$$

Oxygen.—Pass the gas into the pyrogallate pipette 12 times, read and record volume. If the volume does not remain constant after 12 passes, the solution should be renewed.

$$\text{Percentage of oxygen} = \frac{\text{Contraction} \times 100}{\text{c.c. of sample taken.}}$$

Carbon Monoxide, Hydrogen, and Methane.—Pass the gas slowly through the cuprous chloride pipette *g* several times to remove the bulk of the carbon monoxide, and then into KOH pipette to remove acid vapors. Return the sample to the burette, adjust the compensator level to the mark, and read the volume. The contraction in cubic centimetres is the volume of carbon monoxide absorbed by cuprous chloride, and is to be added to the remainder of the carbon monoxide determined later by combustion, to get the total volume of carbon monoxide in the sample.

Turn cock *h* through 180 degrees, and lower levelling bulb *g*, placing the sample under slightly reduced pressure. Turn cock *r* to communicate with the atmosphere through *f*, and draw sufficient air (approximately 25 c.c. for exhaust gases) into the burette to burn all the combustibles in the sample. Adjust the compensator and read the total volume. Turn cocks *r* and *h* 180 degrees, open cock t'''', and pass the mixture into the combustion pipette *s* by lowering bulb *v* and raising *g*. Close the switch *w*, and raise the temperature of the platinum wire to a bright yellow. Pass the gas back and forth over the hot platinum wire by raising and lowering the levelling bulb *g*, at the same time moving the levelling bulb *v* to keep the surface of the mercury in this bulb on the same level as the mercury in the combustion pipette; keep the combustion pipette cool by playing a stream of compressed air on the upper part of the pipette. After the combustion is complete, cut off the current and allow the pipette to cool, and return the gas to the burette by lowering levelling bulb *g* and raising *v*, bringing the mercury level to the mark o'''' and closing the cock t''''. Read and record the volume. The difference in volumes is the contraction due to combustion.

Pass the gas into the caustic pipette to remove and determine the carbon dioxide formed by combustion. Read and record the difference in volume as carbon dioxide from combustion. Finally pass the gas into the pyrogallate pipette repeatedly to absorb and determine the residual oxygen.

From the CO absorbed by cuprous chloride, the contraction on combustion, the CO_2 from combustion, and the residual oxygen, the total carbon monoxide, hydrogen, and methane are computed as follows:

$$\text{Percentage of hydrogen} = \frac{(\text{Contraction} - \text{oxygen consumed})\ 100}{\text{c.c. of sample taken}}$$

$$\text{Percentage of methane}^{5} = \frac{(\tfrac{3}{2}\text{ contraction} - \tfrac{1}{2}\ CO_2 - \text{c.c.H})\ 100}{\text{c.c. of sample taken}}$$

$$\text{Percentage of carbon monoxide} = \frac{(\text{CO by } CuCl_2 + CO_2 \text{ formed} - \text{c.c. } CH_4)\ 100}{\text{c.c. of sample taken}}$$

The following data sheet of an exhaust gas analysis illustrates the above calculations:

Data Sheet of an Exhaust Gas Analysis.

Car, Hudson — Laboratory No. 11869
Apparatus, Orsat No. 12. — Bottle No. 11 c.c.

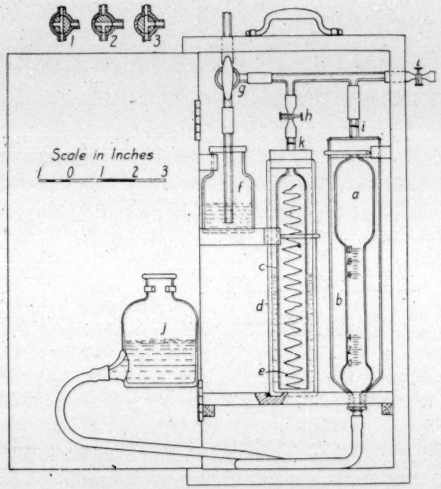
		Burette reading.	Difference.	Per cent.
A	Volume of sample taken	49.90		
B	Carbon dioxide	44.95	4.95	9.9
C	Unsaturated hydrocarbons	—	—	—
D	Oxygen	43.70	1.25	2.5
E	CO by Cu_2Cl_2	41.95	1.75	—
F	Total volume	66.65	—	—
G	Air added	24.70	—	—
H	Equivalent oxygen = Gx0.209	—	5.15	—
I	Volume after burning	64.60	2.05	—
J	Volume after CO_2 absorption	64.20	0.40	—
K	Residual oxygen	60.15	4.05	—
L	Oxygen consumed = H − K	—	1.10	—
M	Hydrogen = I − L	—	0.95	1.9
N	Methane = [(21 − J) ÷ (3 − M)]	—	0.30	0.6
O	CO = J − N	—	0.10	—
P	Total CO = E + O	—	1.85	3.7
S	Nitrogen (By difference)	—	—	81.4
	Determined by difference			

[5] In exhaust gas analyses, the term "methane" really means the volume of methane equivalent to the total hydrocarbons, as other hydrocarbons as gasoline vapor may also be present.

PORTABLE ORSAT APPARATUS FOR DETERMINING CARBON DIOXIDE ONLY.

A simple portable apparatus for determining carbon dioxide only is sufficient for adjusting carburetors and determining the completeness of combustion. Fig. 5 illustrates a compact form of the well-known portable Orsat apparatus modified especially for carbon dioxide determinations on road tests. The entire apparatus weighs five pounds, and the outside divisions are 4½ by 7 by 14 inches.

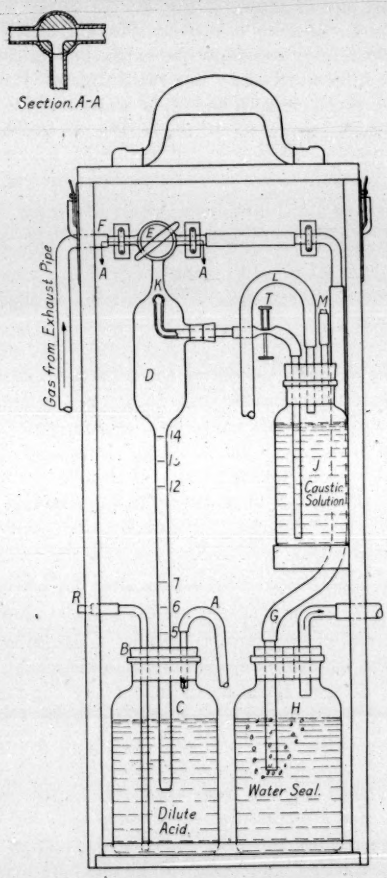
FIG. 5.



Portable Orsat apparatus for analysis of CO_2 in exhaust gas.

The water-jacketed burette *a* has a capacity of 100 c.c., and is graduated on the narrow point to read directly in percentage. Slightly acidulated water is used for the levelling fluid in the bottle *j*. The pipette *d* contains sodium hydroxide solution, containing 20 grams of NaOH in 100 c.c. of water for absorbing the carbon dioxide. The wavy line *e* represents a piece of sheet iron to expose a large surface of hydroxide solution to the gas. At *g* is a three-way glass cock, and *f* is a water-seal through which a rapid stream of exhaust gas is allowed to bubble while taking

FIG. 6.

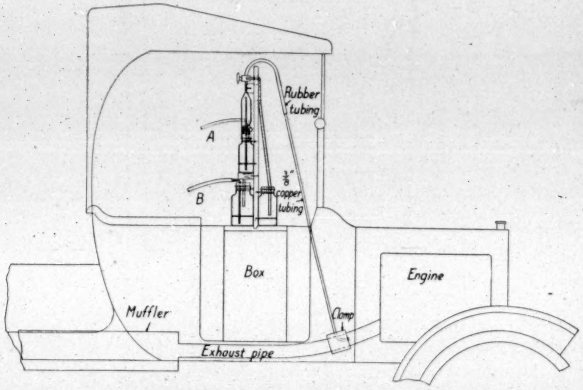


Details of portable CO_2 indicator.

the sample. The glass tube protruding out of the top of the box is connected with a heavy-walled rubber tube and a copper pipe to the exhaust pipe as shown in Fig. 7.

Procedure in Making a Carbon Dioxide Determination.—Turn *g* to position 1, and allow the exhaust from the engine to bubble through the water-seal *f* in a rapid stream. Raise levelling bottle *j;* open pinch-clamp *i,* and allow water-level in the burette to reach the mark *l* at the top of the burette; close *i,* lower *j,* and

FIG. 7.



Method of connecting indicator to the exhaust for making analyses on the road.

slowly open pinch-clamp *h,* raising the caustic solution to the mark at the top of the caustic pipette. Close *h,* open *i,* and again bring the water-level in the burette to the mark *l* by raising *j;* then close *i.* The apparatus is now ready for taking a gas sample. With one hand raise the levelling bottle *j* to the level of mark *l,* and with the other hand turn *g* to position 3, and slowly lower *j,* thus drawing a small part of the gas stream into the burette. Draw slightly more than 100 c.c. of gas into the burette, then turn *g* to position 1. Raise *j* until the water-level in the burette reaches the zero mark at the bottom; close the rubber tube connecting the levelling bottle and burette by pinching the tube tight with the fingers, and open *i* momentarily to allow the sample in the burette to come to atmospheric pressure.

Raise *j*, and open *h* slowly, forcing the gas into the caustic pipette. Pass the gas back and forth from the burette to the pipette until all the carbon dioxide is absorbed; six passes are usually sufficient. Lower *j* until the caustic potash solution reaches the mark *k*, close *h*, and after allowing the burette to drain one minute, bring the water in the burette and levelling bulb to the same level, and read the burette. This reading is the percentage of carbon dioxide in the sample. The caustic solution must be renewed when the reading does not remain constant on repeating the above operations.

CARBON DIOXIDE INDICATOR FOR AUTOMOBILE EXHAUST GASES.

The apparatus shown in Fig. 6 was especially designed by one of the writers (G. W. Jones) for the quick determination of carbon dioxide in automobile exhaust gases in road tests. This carbon dioxide indicator is of simple leak-proof construction, easy to operate by the layman, and yet accurate to within the required limits for efficiency tests and carburetor adjustment.

The essential feature of this indicator is the burette *D*, in which the carbon dioxide is absorbed from a measured sample of gas by spraying caustic soda solution from the jet *K* against the inside walls of the bulb *D*, thus causing the liquid in bottle *C* to rise in the slender graduated portion of the burette in proportion to the percentage of carbon dioxide absorbed from the sample.

A rugged three-way stopcock *E* with 6 mm. bore is sealed to the top of the burette.

The caustic jet *K* consists of a series of fine holes evenly spaced on the circumference of the end of the tube *K* at an angle of 45 degrees with the horizontal. From the bulb of the burette extends a slender tube of uniform bore graduated directly in percentages of carbon dioxide.

The lower end of the burette extends into the bottle *C* through the rubber stopper *B*. The bottle *C* is filled to the mark *Z* with a 5 per cent. solution of sulphuric acid by removing the glass plug *R* and inserting a piece of glass tubing, the other end of which dips into the reserve supply of the acid solution. The acid is then drawn into bottle *C* by applying suction to the rubber tube *A*. The glass tubing is then removed, and the glass plug is replaced.

The height of solution may vary one-half inch above and below the mark *Z* without effecting the accuracy of the results, but sufficient solution must remain at all times in the bottle to seal the lower end of the burette when filled with liquid ready for taking a sample.

Bottle *J* is filled with a 10 per cent. solution of caustic soda by removing glass plug *M*, and inserting a small funnel in its place. When bottle *J* is filled, the funnel is removed, and the glass plug *M* is replaced. Enough water is poured into bottle *H* to form a water-seal with the rubber tube extending into the bottle from *G*. After the caustic soda solution is blown to the tip of jet *K*, by blowing on rubber tube *L*, and opening pinch-clamp *P*, the indicator is ready for use.

Procedure in Making a CO_2 Determination.—To make an analysis, cock *E* is turned to the position as shown in section *A-A*, and by blowing in rubber tube *A*, liquid is forced into the burette, and when it reaches cock *E*, the same is turned 180 degrees, thus the burette is completely filled with the acid solution.

The copper tubing leading from the exhaust manifold is connected to the indicator at *F* by heavy-walled rubber tubing. The pressure is sufficient to force a stream of gas from the muffler through cock *E*, and out through the water-seal *H*. When the line has been purged with gas, a sample is taken into the indicator by turning cock *E* 90 degrees to the left, thus allowing the liquid in the burette to fall and pull in a sample of gas, the pressure on the line forcing the gas out through the bottom of the burette into bottle *C*. Cock *E* is then turned 90 degrees to the right, and the gas in the burette is allowed to stand 30 seconds to permit it to come to the surrounding temperature, also to allow the burette to drain. Allowing the gas to stand and cool draws some liquid from *C* into the bottom of the burette, owing to contraction of the gas on cooling. At the end of 30 seconds, cock *E* is turned to the left, and enough gas is allowed to enter the burette to bring the gas volume to the bottom; *E* is then turned 90 degrees to the right. There is now a definite measured volume of gas in the burette at the same temperature as the indicator. Caustic soda is forced into the burette from the jet *K* by blowing on *L*, and at the same time opening pinch-clamp *P*. Six or more separate small charges of the caustic solution are forced into the burette in succession, allowing sufficient time for this solution to drain

TABLE III.

Laboratory Check between Portable and Orsat Apparatus.

Sample No.	CO_2 by indicator, per cent.	Average.	CO_2 by Orsat, per cent.
	11.8		
	12.4		
1	12.3		
	12.6		
	12.6	12.4	12.4
			Average error, % = 0.0
			Maximum error, % = 0.6
	10.8		
	11.7		
2	11.6		
	10.8		
	11.6		
	11.7	11.4	11.0
			Average error, % = 0.4
			Maximum error, % = 0.6
	8.3		
	8.5		
3	8.7		
	8.7		
	8.8	8.6	8.5
			Average error, % = 0.1
			Maximum error, % = 0.3
	7.4		
4	7.3		
	7.5	7.4	7.4
			Average error, % = 0.0
			Maximum error, % = 0.1

down the burette before the next charge is introduced. (An interval of ten seconds between each charge has been found sufficient.) If more time is allowed, the CO_2 is removed before the sixth charge is introduced, but the same result is obtained. The caustic soda solution sprayed into the burette quickly removes the CO_2, and the solution in *C* rises into the stem of the burette to a height depending upon the amount of CO_2 present. The highest point reached by the solution after the sixth charge has been introduced is the correct reading.

The indicator is made ready for another analysis by again blowing into tube *A*, and filling the burette as previously directed. When forced into the burette, the dilute sulphuric acid in *C* neutralizes the caustic soda solution each time, so there is no absorption of CO_2 while the sample is being taken and brought to the surrounding temperature.

A small quantity of solution is blown each time over into bottle *H* when the burette is filled, so that the liquid height in *C* is kept approximately at the level *Z*.

A few drops of phenolphthalein solution is added to the caustic soda solution, which turns pink the solution in *C* when it becomes exhausted.

The bottle *J* holds a sufficient caustic solution to make from twenty-five to thirty-five determinations, depending on how economically the solution is used.

TABLE IV.

Operation Check between Portable and Orsat Apparatus.

Sample.	Grade.	CO_2 by indicator, per cent.	CO_2 by Orsat, per cent.
1-A	Level	7.5	7.1
2-A	Level	10.0	9.1
3-A	Level	8.5	8.4
1-B	Level	12.5	13.1
2-B	Level	11.5	11.4
3-B	Level	11.0	10.9
1-C	3 per cent.	13.5	13.6
2-C	3 per cent.	13.8	13.3
3-C	3 per cent.	13.8	13.2
Average	——	11.3	11.1
Average error, per cent.			0.2
Maximum error, per cent.			0.9

It is important when the first charge of caustic soda solution is blown into the burette that only enough pressure is applied to barely cause the caustic solution to run down the sides of the jet, otherwise a small bubble of gas will be blown out of the bottom of the burette, and this in turn will give too large a percentage indication for carbon dioxide.

Accuracy of Indicator.—The accuracy of the indicator when operated under laboratory conditions is shown by the following results. (CO_2 and air mixture were prepared of varying concentrations and determinations made with the indicator. The CO_2 content was then checked by analyses on an Orsat gas apparatus.)

Table IV shows the accuracy that may be expected while adjusting carburetors on the road: (An automobile was operated at approximately 15 miles per hour on both level and 3 per cent. grades. One sample of the gas was taken into the indicator and analyzed directly for CO_2. Another was taken at the same time for laboratory analysis by the Orsat method.)

From Table IV it is seen that the average error during tests on the road is 0.2 per cent. when several samples are taken, and that individual samples may be in error as much as 1.0 per cent. In general, the individual determinations of the indicator may be regarded as accurate within 0.5 per cent. in most instances on road tests, and more accurate than this when, as should be done, a number of determinations are made and an average taken.

To determine how much the exhaust gas may vary on road tests under constant conditions, an automobile was run over a one-mile curve and up a 3 per cent. grade at 15 miles per hour. Arrangements were made so that three grab samples of the exhaust gas could be taken, also one continuous sample over the entire test period. Three grab samples were taken during each test and the following results were obtained:

Test No.	CO_2, per cent. Grab sample No. 1	No. 2	No. 3	Average of grab samples, per cent.	Continuous samples, per cent.	Average variation, per cent.	Maximum variation, per cent.
1	9.9	9.0	9.4	9.4	9.3	0.1	0.6
2	8.8	9.7	9.1	9.2	9.0	0.2	0.7
3	9.4	9.4	8.5	9.1	9.1	0.0	0.6

All three of the above tests were made under the same conditions, and without changes in carburetor adjustments. It will be seen that the continuous samples vary for the three tests by 0.3 per cent., and therefore it is impracticable to use an apparatus more accurate than 0.3 per cent., as duplicate tests may give percentages of CO_2 which may vary by the above amount. This

applies for continuous samples taken over an estimated time period. In the case of grab sampling, the variation of the exhaust gas is much greater, as shown. In one case the maximum variation equalled 0.7 per cent.

METHOD OF SAMPLING EXHAUST GAS FOR CO_2 DETERMINATIONS.

The procedure to follow in adjusting a carburetor by gas analysis depends upon the type of carburetor, and conditions under which the automobile or truck is usually operated. In every case, the final adjustment should be under actual operating conditions at speeds comparable to that at which the motor vehicle is operated. An exhaust sampling pipe should be fitted as previously described.

The exhaust gas coming from the engine under a slight pressure forces some of the gas out through the copper tube. This copper tube connects with the CO_2 indicator or portable Orsat—as the case may be—by a heavy-walled rubber tube. By putting the exhaust sampling tube in the position shown in Fig. 7, the floor boards in the front seat can be removed and the copper tube brought directly upward to the testing apparatus. A box of about 12-inch cross-section and 18 inches high is convenient for supporting the apparatus while making the tests. If the road over which the motor vehicle is operated is very rough, a 2 or 3-inch pad of cotton waste should be placed between the apparatus and the box to take up the vibration.

The motor vehicle to be tested should be driven two or three miles to get it thoroughly warmed up, then run at a speed at which it is usually operated, and several samples of the exhaust gas should be analyzed and recorded, after which it can be tested at other speeds in a similar manner. Should the percentage of CO_2 be low (especially below 10 per cent.), the carburetor adjustment should be made leaner and the tests repeated. The procedure is continued until the percentage of CO_2 is as high as possible, and still give flexible operation.

A definite value for the percentage of CO_2 that should be in the exhaust gas can not be given to apply to all makes of cars, and especially carburetors. Weather conditions also affect the adjustments. For example, the carburetor may be adjusted to give 13 per cent. CO_2 on a warm summer day, and left at this

adjustment; a sudden change to colder weather may increase the viscosity of the gasoline so as to cause the mixture to be too lean for flexible operation.

In general, 12 per cent. of CO_2 or more in the exhaust is not too high a figure for smooth operation and economy of gasoline. When it is seen that most automobiles and trucks operate under conditions where the exhaust gas contains 9.5 per cent. of CO_2 or less, the adjustment of carburetors by exhaust gas analysis becomes very important.

INTERPRETATION OF EXHAUST GAS ANALYSIS.

Automobile exhaust gas consists of carbon dioxide, oxygen, carbon monoxide, hydrogen, methane, gasoline vapor, nitrogen, and traces of unsaturated hydrocarbons.

Carbon Dioxide.—This gas is formed by complete combustion of carbonaceous material. The amount of carbon dioxide in exhaust gas depends upon a number of factors, chief of which are the ratio of air to gasoline vapor (carburetor adjustment), thoroughness of mixing vapor and air, completeness of vaporization, and temperature and degree of compression in the cylinders. Under ideal conditions with the theoretical amount of air for complete combustion of the gasoline, the only products of the reaction or combustion should be carbon dioxide, water vapor, and nitrogen. The nitrogen comes from the air used for combustion. If an excess of air be present, the combustion products are carbon dioxide, water vapor, oxygen, and nitrogen. However, under practical operating conditions there is usually a small percentage of oxygen passing through into the exhaust gases, even when a deficiency of air is mixed with the gasoline vapors. The maximum possible percentage of carbon dioxide is formed in the exhaust gas when the theoretical amount of air is present, and there is perfect combustion of the hydrogen and carbon of the gasoline. This value varies slightly with the percentages by weight of carbon and hydrogen in the gasoline. Assuming a gasoline of 84 per cent. carbon and 16 per cent. hydrogen, then

	CO_2 lb.	H_2O lb.	N_2 lb.
0.84 lb. of carbon produces	3.08	—	7.43
0.16 lb. of hydrogen produces	—	1.44	4.25
Total of	3.08	1.44	11.68

The water condenses out and is not indicated in the exhaust gas analysis. Changing from a weight to a volumetric basis, by dividing by the molecular weights, we have

$$\frac{11.68}{28} = 0.417$$

$$\frac{3.08}{44} = 0.070$$

$$\text{Total} = 0.487$$

$$\frac{0.070}{0.487} \times 100 = 14.4 \text{ per cent. carbon dioxide by volume.}$$

$$\frac{0.417}{0.487} \times 100 = 85.6 \text{ per cent. nitrogen by volume.}$$

The maximum carbon dioxide content that can be obtained in the exhaust gases when the above gasoline is used is 14.4 per cent. When the exhaust gas indicates this value for carbon dioxide, the combustion is complete. Lower values are due either to incomplete combustion or excess air.

Oxygen.—This may be due to excess air (lean mixture), large excess of gasoline vapor (very rich mixture), incomplete vaporization, or poor mixing of the gasoline vapor and air in the engine. If the gasoline is not completely vaporized and is partly carried into the cylinder in the form of a mist consisting of small globules of liquid gasoline, the combustion is incomplete, especially at low speeds and before the engine gets warmed up. The oxygen cannot attack the gasoline in the interior of these particles in the short time interval of the explosion in the cylinder. This condition gives rise to free oxygen in the exhaust gases, together with high percentages of incomplete combustion products such as carbon monoxide, hydrogen and methane.

Carbon Monoxide.—This is the poisonous constituent of exhaust gases, and is formed by incomplete combustion of carbon. Unless an excess of air is present, and the gases are properly vaporized and mixed, carbon monoxide is produced in varying large quantities. Carburetor adjustment for feeding a rich mixture is the most general cause for the large quantities of carbon monoxide formed in the exhaust of most machines. The mixture may be so rich that the ignition takes place only in the neighborhood of the spark, and does not propagate itself throughout the whole charge. This condition produces large quantities of carbon monoxide and other unburned gases, such as hydrogen

and methane, together with oxygen and gasoline vapor. Experiments made by Burrell[6] showed that when a mixture of 5 per cent. gasoline-vapor in air was exploded, 9 per cent. of unconsumed oxygen remained in the residual gases, and the flame travelled so slowly that it could be followed by the eye. When 4.1 per cent. gasoline-air mixtures were exploded, 3.4 per cent. of oxygen was found. This substantiates the fact that when rich mixtures are used in gasoline engines there may be large quantities of oxygen present in the exhaust gases accompanied by products of incomplete combustion.

The presence of carbon monoxide in automobile exhaust gases is not only objectionable on account of its poisonous nature, but it means a material loss in mileage per gallon of gasoline used. The average analysis of exhaust gas from the 101 cars and trucks tested by the Bureau of Mines showed about 6.5 per cent. carbon monoxide. This means that 30 per cent. of the heat in the gasoline was lost. With proper combustion in the engine, and correct carburetor adjustment, at least 20 per cent. greater mileage should have been secured per gallon of gasoline used. One of the cars was exhausting 13.2 per cent. of carbon monoxide, which corresponds to a loss of 50 per cent. of the gasoline used—an enormous and unnecessary waste of gasoline.

Hydrogen and Methane.—The hydrogen and methane in exhaust gases are the result of the decomposition of the gasoline in the absence of oxygen, and perhaps in a lesser degree to reactions in which water-vapor takes part. In a general way, the hydrogen increases proportionally with the carbon monoxide; and at adjustments at maximum power equals approximately 40 per cent. of the CO content. The percentage of methane is very low when the engine is running under the best conditions.

Gasoline Vapor.—The gasoline vapor in exhaust gases is due to poor ignition, poor mixing, and incomplete vaporization of the gasoline and air; also to rich mixtures, or incomplete flame propagation. One or several of these above conditions may cause small portions of the gasoline to pass through the engine without reacting with the oxygen present in the air.

[6] Hood, O. P., Kudlich, R.H., and Burrell, G. A., "Gasoline Mine Locomotives in Relation to Safety and Health," Bull. 74, Bureau of Mines, 1915, pp. 69-71.

In the gas analyses, the gasoline vapor and all other hydrocarbons appear as methane. The analysis gives the equivalent methane value for all the hydrocarbons in the exhaust gas, and the result is correct as regards carbon content for computing the total volume of exhaust gases from the gasoline consumption and the carbon content of the gasoline. The determination of gasoline vapor as methane causes the hydrogen value in the analysis to be somewhat less than its true value. This error in the hydrogen value has no effect on calculation of the true volume of carbon monoxide, carbon dioxide, and methane equivalent of hydrocarbons produced in the tests.

Finally, it must be recognized that absolutely all the gasoline fed into the engine does not appear in the exhaust gas analysis. In cylinders with poorly fitting piston rings, and in very cold weather, some gasoline escapes into the crank-case, also traces of carbon remain behind on the cylinder walls. To partly compensate for this loss, some constituents of the exhaust gas undoubtedly came from the burning of lubricating oil in the cylinders.

Unsaturated Hydrocarbons.—These appear in exhaust gases at times, especially when the carburetor has a very rich adjustment. The exhaust gases in the road tests cited above were tested from time to time for unsaturated hydrocarbons. The amount present usually was not more than 0.1 per cent., the experimental error of analysis. In exceptional cases, where a very rich mixture was used, and the car was in poor adjustment, the percentage of unsaturated hydrocarbon was as high as 1 per cent. In order to keep the exhaust gas calculations correct, the unsaturated hydrocarbon value was doubled and reported as methane.

COMPUTATION OF VOLUME OF EXHAUST GASES.

Volume of Exhaust Gases.—The total volume of exhaust gases produced per gallon of gasoline consumed may be computed from the analysis of the exhaust gases and the weight and analysis of the gasoline. This computation is based on the assumption that all the carbon in the gasoline appears in the exhaust gases. As a matter of fact, there is a small error due to solid particles of carbon in the exhaust and on the motor surfaces, and leakage of gasoline into the crank-case. This error may be partly compensated, or exceeded in some cases, by lubri-

cating oil burning in the cylinders. The total error is negligible, as shown by tests made with engine idling, in which the exhaust gases were collected and measured in a 50 cubic foot calibrated gas tank. The measured volumes checked to within 1 per cent. of the volumes computed from the analysis in the usual manner, when the average of four tests were taken and the maximum variation was 6 per cent.

COMPUTATION OF VOLUME OF EXHAUST GASES.

From the gasoline analysis:

a = sp. gr. of the gasoline at 60° F.

b = per cent. carbon in the gasoline by weight.

8.33 = weight of one gallon water, in pounds, at 60° F.

(1) $8.33ab$ = pounds of carbon in one gallon of the gasoline.

From the gas analysis:

c = per cent. CO_2 in the exhaust gas by volume.

d = per cent. CO in exhaust gas by volume.

e = per cent. CH_4 in exhaust gas by volume.

0.1158 = weight in lb. of 1 cu. ft. CO_2, 65° F. and 29.92 in. Hg.

0.0732 = weight in lb. of 1 cu. ft. CO, 65° F. and 29.92 in. Hg.

0.0420 = weight in lb. of 1 cu. ft. CH_4, 65° F. and 29.92 in. Hg.

$0.1158 \times 3/11^{r} = 0.0316$ = lb. carbon in 1 cu. ft. CO_2 at 65° F. and 29.92 in. Hg.

$0.0732 \times 3/7^{r} = 0.0314$ = lb. carbon in 1 cu. ft. CO at 65° F. and 29.92 in. Hg.

$0.0420 \times 3/4^{r} = 0.0315$ = lb. carbon in 1 cu. ft. CH_4 at 65° F. and 29.92 in. Hg.

$0.0316c + 0.0314d + 0.0315e$ = total pounds of carbon in 1 cubic foot of exhaust gas. This expression may be simplified by using the mean value 0.0315 as follows:

(2) $0.0315\ (c + d + e)$ = total pounds of carbon in 1 cubic foot of exhaust gas.

Dividing by (1) and (2)

$$\frac{8.33\ ab}{0.0315\ (c + d + e)} = \frac{264.4\ ab}{c + d + e} = \frac{\text{cu. ft. exhaust gas at 65° F.}}{\text{29.92 in. of Hg. per gallon of gasoline.}}$$

The expression $264.4ab$ is constant for each gasoline, and represents the total cubic feet of carbon-containing gases (CO, CO_2, and CH_4) that is produced by gasoline of a given specific gravity and carbon content. The expression $c + d + e$ varies with each test, and represents the proportion by volume of carbon-containing gases in one cubic foot of exhaust gas.

[r] Ratio of atomic weight of carbon to molecular weight of gas.

Computation of Pounds of Air Supplied Per Pound of Gasoline.—The pounds of air supplied per pound of gasoline is computed in the following manner:

Cubic feet of exhaust gas per gallon of gasoline ÷ (weight of 1 gallon of gasoline = 8.33 × specific gravity at 65° F.) = cu. ft. of exhaust gas per pound of gasoline = A.

A × per cent. of nitrogen in exhaust gas = total cubic feet of nitrogen supplied per pound of gasoline used = B.

B ÷ 0.79 (per cent. nitrogen in air by volume) = cu. ft. of air supplied per pound of gasoline = C.

C × 0.07572 [8] = lb. of air supplied per pound of gasoline.

Percentage Completeness of Combustion.—The percentage of the total heat of the gasoline lost due to the presence of combustible gases in the exhaust, may be calculated by either of two methods, namely, (1) the use of the quantity and calorific value of the combustible gases in the exhaust, also the calorific value of the gasoline used, and (2) the use of the analysis of the exhaust gas and gasoline.

Computation of Percentage Completeness of Combustion.—Calculation of this item by the quantity and calorific value method as applied to the average results of twenty-three cars tested on level grade is as follows:

Average Composition of Exhaust Gas, by Volume from Tests of 23 Cars, at 15 Miles per Hour Level Grade.

	Per cent.
Carbon dioxide	8.9
Oxygen	2.3
Carbon monoxide	6.3
Methane	0.9
Hydrogen	3.0
Nitrogen	78.6
	100.0

Cubic feet of exhaust gases at 65° F. and 29.92 inches Hg. = 988 (from test data).

Composition of Gasoline.

Specific gravity	0.713
Carbon, per cent.	84.3
Hydrogen, per cent.	15.7
Calorific value, B.t.u. per lb.	21,300.
Calorific value, B.t.u. per gal.	130,000.

[8] Weight of 1 cu. ft. of air at 65° F. and 29.92 in Hg.

Exhaust gas from one gallon of gasoline on level grade tests contains:

$$988 \times 0.063 = 62.2 \text{ cubic feet CO}$$
$$988 \times 0.009 = 8.9 \text{ cubic feet } CH_4$$
$$988 \times 0.030 = 29.6 \text{ cubic feet H}$$

Total heat in unburned gases per gallon gasoline:

$$62.2 \times 320^9 = 19{,}900 \text{ B.t.u.}$$
$$8.9 \times 1000 = 8{,}900 \text{ B.t.u.}$$
$$29.6 \times 322 = 9{,}600 \text{ B.t.u.}$$
$$38{,}400 \text{ B.t.u.}$$

$$\frac{38{,}400}{130{,}000} = 29.5 \text{ per cent.}$$

Therefore, 29.5 per cent. of the total heat of the gasoline goes out in the exhaust in the form of combustible gases—in other words, the completeness of combustion is 100 − 29.5, or 70.5 per cent.

By gasoline and exhaust gas analysis this item is calculated directly from the exhaust gas and gasoline analysis as follows:

From gasoline analysis by weight:

$$\frac{\text{Per cent. hydrogen} \times \frac{1}{2}}{\text{Per cent. carbon} \times \frac{1}{12}} = \text{Ratio of water vapor to carbon dioxide, by volume on complete combustion} = A.$$

Assuming the heat of combustion of carbon as 14,540 B.t.u., and hydrogen as 62,000 B.t.u., then

$$\frac{14{,}540 \times \%\text{ carbon}}{(14{,}540 \times \%\text{ carbon} + (6200 \times \%\text{ hydrogen})} = \%\text{ heat units due to carbon} = B.$$

$$\frac{62{,}000 \times \%\text{ hydrogen}}{(14{,}540 \times \%\text{ carbon} + (6200 \times \%\text{ hydrogen})} = \%\text{ heat units due to hydrogen} = C.$$

From gas analysis by volume:

$$\%\,CO_2 + \%\,CO + \%\,CH_4 = \text{volume of } CO_2 \text{ formed on complete combustion} = D.$$

$$\frac{\%\,CO_2 + (0.3 \times \%\,CO)}{\%\,CO_2 + \%\,CO + \%\,CH_4} = \text{Completeness of combustion of carbon} = E.$$

0.3 = Proportion of heat liberated in burning carbon to CO.

$D \times A$ = Equivalent volume of water vapor formed on complete combustion.

$$1 - \frac{\%\,H_2 + (2 \times \%\,CH_4)}{D \times A} = \text{Completeness of combustion of hydrogen} = F.$$

[9] Gross B.t.u. per cu. ft. at 65° F. and 29.92 inches Hg.

Hence, the completeness of combustion of gasoline $= (B \times E) + (C \times F)$.

The factors A, B, and C are constant for any given grade of gasoline.

The following example explains this method:

Composition of Exhaust Gas by Volume.

	Per cent.
Carbon dioxide	9.0
Oxygen	0.5
Carbon monoxide	7.9
Methane	0.6
Hydrogen	3.7
Nitrogen	78.3
	100.0

Composition of Gasoline by Weight.

	Per cent.
Carbon	84.3
Hydrogen	15.7

Applying equations A, B, C, D, E, and F.

$$A = \frac{15.7 \times \frac{1}{2}}{84.3 \times \frac{1}{12}} = 1.12$$

$$B = \frac{14{,}540 \times 84.3}{(14{,}540 \times 84.3) + (62{,}000 \times 15.7)} = 56 \text{ per cent.}$$

$$C = \frac{62{,}000 \times 15.7}{(14{,}540 \times 84.3) + (62{,}000 \times 15.7)} = 44 \text{ per cent.}$$

$$D = 9.0 + 7.9 + 0.6 = 17.5 \text{ per cent.}$$

$$E = \frac{9.0 + (0.3 \times 7.9)}{9.0 + 7.9 + 0.6} = 65 \text{ per cent.}$$

$$D \times A = 19.6 \text{ per cent.}$$

$$F = 1 - \frac{3.7 + (2 \times 0.6)}{19.6} = 75 \text{ per cent.}$$

$$\begin{aligned} \text{Completeness of combustion} &= (B \times E) + (C \times F) \\ &= (56 \times 65) + (44 \times 75) \\ &= 69 \text{ per cent.} \end{aligned}$$

THE STABILITY OF ATOM NUCLEI, THE SEPARATION OF ISOTOPES, AND THE WHOLE NUMBER RULE.*

BY

WILLIAM D. HARKINS, PH.D.

Department of Chemistry, University of Chicago.

40. RUTHERFORD'S DIRECT EXPERIMENTAL EVIDENCE FOR THE HARKINS-WILSON THEORY OF NUCLEAR STRUCTURE.

AN extremely large amount of experimental evidence in favor of the helium-hydrogen theory has been presented in the preceding 39 sections of the present paper. This evidence includes such a large number of facts that it is difficult to comprehend their importance, and even scientific men often take the unscientific attitude that a large number of facts of a varied character are not so convincing as a single fact, which is due to the difficulty of obtaining a comprehensive understanding of a great number of facts without subjecting them to an intensive study. It is therefore of interest that very simple and direct evidence in favor of the theory has been obtained by Rutherford.[42]

In their first outline of the hydrogen-helium theory Harkins and Wilson advanced the idea[43] *that the alpha particle is so extremely stable that no nucleus built of alpha particles alone—that is, no atom whose atomic weight is divisible by 4—could be expected to give hydrogen in a disintegration, but that this might be possible when hydrogen nuclei other than those contained in alpha particles are present, that is when the atomic weight is not divisible by 4.* In direct confirmation of this idea Rutherford found only four years later that in the artificial bombardment of atoms by alpha particles *hydrogen is not given off* from atoms whose atomic weight is divisible by 4, but is given off from certain light atoms whose weights are $4q+3$ and $4q+2$, if q is a whole number.

Rutherford's remarkable results depend upon the extremely high amount of kinetic energy possessed by the fast-moving alpha

* Continued from page 535, vol. 194, October, 1922.

[42] "Artificial Disintegration of the Elements," *J. Chem. Soc.*, **121**, 400–15 (1922), Rutherford and Chadwick, *Phil. Mag.*, **42**, 809–825 (1921), **44**, 417–32 (1922).

[43] *J. Am. Chem. Soc.*, **37**, 1393 (1915), *Phil. Mag.*, **30**, 723–34 (1915).

particles ejected from such radioactive substances as radium-C or thorium-C, which is found to be sufficient to disintegrate the nuclei of certain types of atoms. The high-speed alpha particles from thorium-C have a velocity of more than 16,000 miles per second, or about 32,000 times that of a swift rifle bullet. Thus the energy, mass for mass, is about one billion times greater than that of the bullet. When such alpha particles are shot through hydrogen, or through any compound containing hydrogen, they in some cases collide with the nuclei of hydrogen atoms, and give to the latter a velocity as high as one and six-tenths times that of the alpha particle.

The alpha particles from radium-C have a velocity of about 12,000 miles per second, and produce the same general effects as the ones from thorium-C. Those from the former substance have a range of 7 cm., but the range of the hydrogen nuclei with which they collide is of the order of 28 cm. and almost none of them has a range as high as 30 cm. Either the alpha particles or the swift H-nuclei may be detected by the scintillations [44] which they produce on a zinc sulphide screen, provided the latter is put within the range of the particles. While a few fast-moving hydrogen particles are detected in oxygen, it is evident that these arise from a slight contamination of the source with hydrogen.

The effect of such a contamination may be eliminated by putting the screen at a distance corresponding with a range of 30 cm., at which range no scintillations from hydrogen can be detected. However, in order to make certain that no particles from hydrogen itself or its compounds are detected, the screen was placed at a distance corresponding with a range of 32 cm. At this distance no scintillations were detected in oxygen, hydrogen, or in carbon dioxide and hydrogen mixed, but they were found when the alpha particles were shot through substances containing boron (58), nitrogen (40), fluorine (65), sodium (58), aluminium (90), or phosphorus (65). The figures in parenthesis give the forward ranges of the particles given off for the respective ele-

[44] The paths of such H-particles are easily visible in the Shimizu-Wilson apparatus [*Proc. Roy. Soc.*, London (A) **99**, 425 (1920); *Electrician*, **86**, 720 (1921); *Engineering*, **111**, 692 (1921)] devised for making visible the tracks of alpha particles, as has been found in an experiment by R. W. Ryan and the writer, who are engaged in a photographic study of atomic disintegrations by the use of this apparatus.

ments, and it is seen that these greatly exceed the range of those projected in hydrogen itself, being more than three times as great in the case of aluminium.

The nature of the particles ejected from these elements was determined by comparing them with the long-range particles in hydrogen, and it was found that both were deflected to the same extent in a strong magnetic field, and behaved like swift H-nuclei carrying a single positive charge. The maximum speed of the hydrogen nuclei shot off from the different atom nuclei may be calculated by assuming the law which connects the velocity and range of alpha particles according to which the velocity is proportional to the cube root of the range. The maximum speed imparted to a free H-nucleus by collision with an α-particle of velocity V has been calculated to be $1.6\,V$, while its range in air is about 28 cm. Accordingly the maximum velocity of the H-particle from nitrogen is $1.8\,V$, while that from aluminium of range 90 cm. is $2.37\,V$. The term "free hydrogen nucleus," as used here, refers to the nucleus of any hydrogen atom, whether in hydrogen itself or in any compound of hydrogen, but does not indicate a proton combined in any complex atom. The energy of chemical attachment is so small in comparison with that of nuclear binding, that any nucleus which is united only to planetary electrons may be considered as free in the sense of the investigation under discussion.

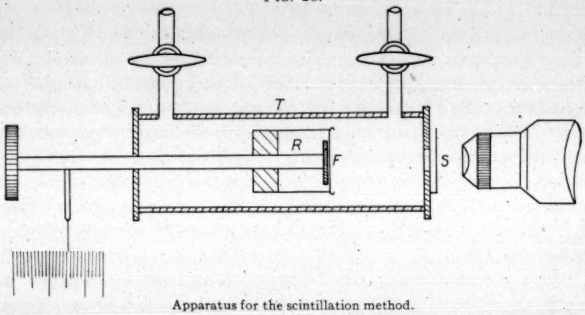
In a direct collision the α-particle communicates 0.64 of its energy to a free H-nucleus, and all H-nuclei which have a range greater than 56 cm. are projected with an energy greater than that of the alpha particle which ejects them, as is the case when they are driven out of phosphorus or aluminium. With the latter the maximum energy of the H-nucleus is 1.4 times that of the colliding α-particle. Thus, at least with these two atomic species, a part of the energy is derived from the nucleus which disintegrates. This is somewhat similar to what is found in the radioactive elements, where all of the energy is supposed to come from the disintegrating nucleus. In either case it is probable that a large part of the velocity and kinetic energy are gained in passing through the highly repulsive field just outside the complex nucleus.

The amount of disintegration produced in these experiments is exceedingly minute. The α-particle from radium-C passes

through the planetary electronic systems of about 100,000 atoms of aluminium, but only about one particle in five hundred thousand gets near enough to the aluminium nucleus to effect the liberation of a H-nucleus. The collected α-particles from a gram of radium amount to 163 cubic millimetres of helium per year, so the amount of hydrogen liberated cannot be more than 1/1000 of a cubic millimetre per year. Thus the amount of hydrogen liberated in any practicable experiment is not detectable by ordinary chemical methods, but the disintegration may be studied by any means which will detect *individual* swift-moving H-nuclei.

The apparatus used by Rutherford in this work is extremely simple, and consists merely of a brass tube T (Fig. 20), 3 cm. in

FIG. 20.



Apparatus for the scintillation method.

diameter, provided with stopcocks which permit the circulation of dry gases. At the end toward the microscope is a hole covered with a very thin silver foil. The zinc sulphide screen, S, is put 1.3 mm. away from the hole in order to leave room for the admission of mica screens over it. The radioactive source, R, is fitted at the end of a rod in order that its distance from the screen may be easily varied. Directly in front of this is fastened the substance, F, to be bombarded, if it is a solid. The silver foil and the mica plates are used to reduce the distance traversed by the H-nuclei. The stopping power for alpha particles of any species of atoms is proportional to the two-thirds power of its atomic number,[45] and the number of atoms per unit distance in a solid is enormously greater than in a gas; so the actual distance traversed by an

[45] Glasson: *Phil. Mag.*, **43**, 478 (1922).

H-nucleus, of range 28 cm. in air, is very small in a solid, particularly if the atomic number of its atoms is high. Aside from the additional convenience of a small apparatus, it is important to reduce the actual distance traversed by the alpha and H-particles as greatly as is possible, since the number of scintillations would decrease as the square of the distance between the source and the screen increases, in the case of particles of infinite range. Thus if the actual distance is 3.5 cm. the amount of radium required for the experiment is only about one-eightieth of that required at a distance of 32 cm.

A typical experiment is described by Rutherford as follows: "Suppose that the radioactive source, consisting of a brass disk coated on one side with an invisible layer of radium-C corresponding in γ-ray activity to 40 mgs. of radium, is placed 3.5 cm. from the screen and that a current of dry hydrogen is passed through the apparatus. Suppose the stopping power of the materials between the source and the zinc sulphide screen corresponds to 20 cm. of air. The passage of the α-particles, which in this case have a range of 7 cm., through the hydrogen, liberates a large number of high-speed H-atoms, which produce scintillations on the screen. Their number with the microscope described (as having a field of 40 sq. mm.) is so great—thousands per minute—that it would be impossible to count them without reducing the activity of the source. As additional screens of mica are added, the numbers fall off rapidly, and for an absorption, say, of 30 cm., not a single H-scintillation can be observed per minute. A similar effect is shown if oxygen is substituted for hydrogen, and a thin strip of paraffin wax or other hydrogen-containing substance is placed over the source. The number of H-scintillations observed for a certain absorption depends only upon the amount of hydrogen, and is quite independent of chemical combination. This is to be expected, for the forces required to set the hydrogen nucleus in rapid motion are enormous compared with the weak forces involved in chemical combination. We thus conclude that, for α-particles of range 7 cm., no H-atoms from hydrogen in the free state or in chemical combination can be detected for an absorption greater than 30 cm. of air.

"The oxygen, which gives no scintillations, is now replaced by dry air. At once for an absorption of 30 cm., we observe more than 100 scintillations per minute when for hydrogen we

did not observe one. By adding mica screens we find that the scintillations cease for an absorption of 40 cm. It is clear that these particles from nitrogen have a greater range than free H-atoms bombarded by α-rays, so the effect observed beyond 30 cm. cannot be ascribed to any hydrogen impurity in the nitrogen.

"The air is now replaced by neutral oxygen, and thin foils of say copper, iron, silver, gold, of stopping power corresponding to about 3 cm. of air, are successively placed over the source. Not a single H-atom can be observed for an absorption of 30 cm. A foil of aluminium is substituted and at once the number of scintillations jumps to more than 100 per minute. Some of the scintillations are very bright, and we find that some of the particles are so swift that the absorption must be increased to 90 cm. before the scintillations vanish."

41. DISCUSSION OF EXPERIMENTS ON ATOMIC DISINTEGRATION.

It has been seen that Rutherford's remarkable experiments, as outlined in the last section, give conclusive evidence in favor of the *Harkins-Wilson theory* of nuclear structure (1915), and are quite as conclusive in showing the invalidity of the *Rutherford theory* (1920) that the light atoms are built up largely of particles of mass 3, a theory Rutherford has now withdrawn. While the experiments show conclusively that hydrogen may be driven out of a complex nucleus, provided it is of a certain type, there still remain a number of important features of the experiments to be investigated. Some of these are listed below:

1. It is of extreme importance to determine the number of hydrogen nuclei liberated in the disintegration of a single atom such as that of aluminium or of nitrogen. The Harkins-Wilson formula for aluminium is He_6H_3, and of nitrogen, He_4H_2, which indicates the *possibility* of three hydrogen nuclei being liberated from a single atom of aluminium, and of two from an atom of nitrogen. It is of value to ask, provided more than one hydrogen nucleus is liberated, does one have a much higher speed than the others, and what are their directions? *

2. Are electrons liberated concomitantly with the protons?

* The high energy of the emitted H-particles seems to indicate that *only one H-particle is emitted.* It may be assumed that this indicates that in the groups $p(pe)$ and $p(pe_2)$ the negative electrons are not able to bind firmly more than their own number of protons.

3. Are electrons emitted in any instance without the liberation of protons?

Five out of the six nuclei from which hydrogen has been driven out have the formula $a\ (\frac{M}{2}-\frac{1}{2})\ p_3e_2$, while that of nitrogen, which gives H-particles only of the shortest range, is a_3p_2e.

It is of interest to introduce here, as in the formulæ just given, the assumption that the number of alpha particles in any nucleus is equal to the *whole number* given by dividing the atomic weight of the species by 4. There is little doubt but that this is justified in general by the evidence. (It is of course *possible* that the number of protons attached in some other way is equal to as much as 4 or even more.) Consideration will now be given to the *formula-groups* which are present in the *composition* of the nuclei on the basis of this assumption. Of these p_3e_2 and p_2e_2 are relatively abundant, pe is somewhat less abundant, and p_2e and pe_2 are rare, as is indicated in Table XXVIII.

TABLE XXVIII.

Formula-Groups, Other Than the Alpha Particle, Present in the Composition of Atom Nuclei.

Group.	Disintegrated to give long-range H-particles?	Present in		Series.
		A. Present in Relatively Abundant Atomic Species.		
p_3e_2	Yes	B_1^{11}, F_1^{19}, Na_1^{23}, Al_1^{27}, P_1^{31}	(Class II)	Lithium
p_2e_2	No	Ne_2^{22}, Mg_2^{26}	(Class I)	Uranium
		B. Present in Moderately Abundant Atomic Species.		
pe	No	Be_1^{9}, Mg_1^{25}, Si_1^{29}	(Class III)	Meta-chlorine
		C. Present Only in Relatively Rare Atomic Species.		
p_2e	Yes	N_0^{14}	(Class IV)	Uranium
pe_2	No	Cl_3^{37}, K_3^{41}	(Class II)*	Meta-chlorine

* Chlorine and potassium have a higher atomic number than any atomic species thus far disintegrated, so the class number may not be in point.

Atomic species of the thorium series, that is those supposed by the theory to have nuclei built of alpha particles, or of alpha particles and cementing electrons, have not been disintegrated, so far as the experimental evidence shows. Rutherford's method, however, does not in any case *reveal* a disintegration which gives particles of a range less than 32 cm. *Thus far only those atoms*

which contain formula-groups in which the number of protons is greater than the number of electrons, have been shown to be artificially disintegrated to give hydrogen nuclei. Even if it is proved later that atoms which show the formula-groups pe, p_2e_2, and pe_2, may be disintegrated to give hydrogen, they will be found to give particles of a shorter range, and thus exhibit less energy of disintegration, unless the present experiments are in error. Neither the p_2e group of Li_0^6 nor the p_3e_2 group of Li_1^7 has been found to give the long-range H-particles. *These facts raise the important question as to whether it is necessary for these groups to contain more protons than electrons if they are to give rise to particles of such a great range.* Unfortunately the number of cases investigated is not great enough to definitely settle this question, but the evidence thus far favors the idea that this is a necessary condition. Table XXIX lists the substances thus far investigated.

It is of interest to note that lithium, with the lowest atomic number, gave no long-range particles, and it is of importance to determine whether it disintegrates at all. The range of the particles given off is the highest for the two elements which have the highest atomic numbers of those which are disintegrated, but is much less for phosphorus than for aluminium. Elements of higher number than 31 (phosphorus) have not been found to give off long-range particles, which may be due to the higher repulsive field around the nuclei of higher charge. This does not allow the penetration of the alpha particle with the retention of such a large amount of kinetic energy; or it may be that the protons become imbedded with alpha particles as the number of the latter increases; or that in some other way the energy of attachment of the protons increases too greatly to allow them to be driven off.

A fact of the greatest interest in the case of aluminium is that nearly as many long-range H-particles are emitted in the backward as in the forward direction of the α-particles, but with a distinctly smaller velocity and range. In the case of nitrogen the chance of liberating a swift H-particle is only 1/20 that of setting a free hydrogen atom in motion.

Table XXIX B gives the distribution of the momentum between the various particles concerned in the disintegration of the atoms, as calculated by Rutherford by the use of the ordinary

laws of mechanics. The momenta are expressed in terms of the initial velocity V of the alpha particle. The initial momentum of the α-particle, and therefore the sum of the momenta of the

TABLE XXIXA.

Range of the H-particles (Protons) Liberated in Rutherford's Experiments on Atomic Disintegration.

(Elements marked "...." gave practically no particles of range greater than 32 cm.)

At. No.	Element.	Species.	Material.	No. of particles per minute per mg. for microscope used.	Maximum range of particles in cm. of air.*
3	Lithium	Li_0^7, Li_1^7	Li_2O	....	.....
4	Beryllium	Be_1^{9-1}	BeO	....	.....
5	Boron	B_1^{10}, B_0^{11}	B	0.15	58—38
6	Carbon	C_0^{12}	Co_2	....	.....
7	Nitrogen	N_0^{14}	Air	0.7	40—18
8	Oxygen	O_0^{16}	O_2	....	.....
9	Fluorine	F_1^{19}	CaF_2	0.4	65—48
11	Sodium	Na_1^{23}	Na_2O	0.2	58—36
12	Magnesium	Mg_0^{24}, Mg_1^{25}, Mg_2^{26}	MgO	....	.....
13	Aluminium	Al_1^{27}	Al, Al_2O_3	1.1	90—67
14	Silicon	Si_0^{28}, Si_1^{30}	Si	....	.....
15	Phosphorus	P_1^{31} and (?)	P (red)	0.7	65—49
16	Sulphur	S_0^{32} and (?)	S, SO_2	....	.....
17	Chlorine	Cl_1^{35}, Cl_2^{37}	$MgCl_2$	....	.....
19	Potassium	K_1^{39}, K_2^{41}	KCl	....	.....
20	Calcium	Ca_0^{40}, Ca_4^{44}	CaO	....	.....
22	Titanium	Ti_4^{48}	TiO_2	....	.....
25	Manganese	Mn_0^{55}	MnO_2	....	.....
26	Iron	Fe_4^{54} (probably Fe_2^{56})	Fe	....	.....
29	Copper	(Probably Cu_0^{63} and Cu_1^{65})	Cu	....	.....
50	Tin	Sn_{16}^{116}, Sn_{17}^{117}, Sn_{18}^{118}, Sn_{19}^{119}, Sn_{20}^{120}, Sn_{21}^{121} (?), Sn_{24}^{122}, Sn_{26}^{124}	Sn	....	.....
47	Silver	(Probably Ag_{15}^{107} and Ag_{16}^{109})	Ag	....	.....
79	Gold		Au	....	.....

* The first figure gives the forward, the second, the backward range in centimetres.

three bodies, after collision, is 4 V. However, if more than one proton is emitted per atom, the number of bodies is greater than three. Momenta in the direction of the incident α-particle are taken as positive, those in the opposite direction as negative. The

percentage energy gained from the nucleus as the result of the disintegration is given in the last column, and in terms of the initial energy of the α-particle.

42. GENERAL PERIODIC SYSTEM OF THE ATOMIC SPECIES (ISOTOPES).

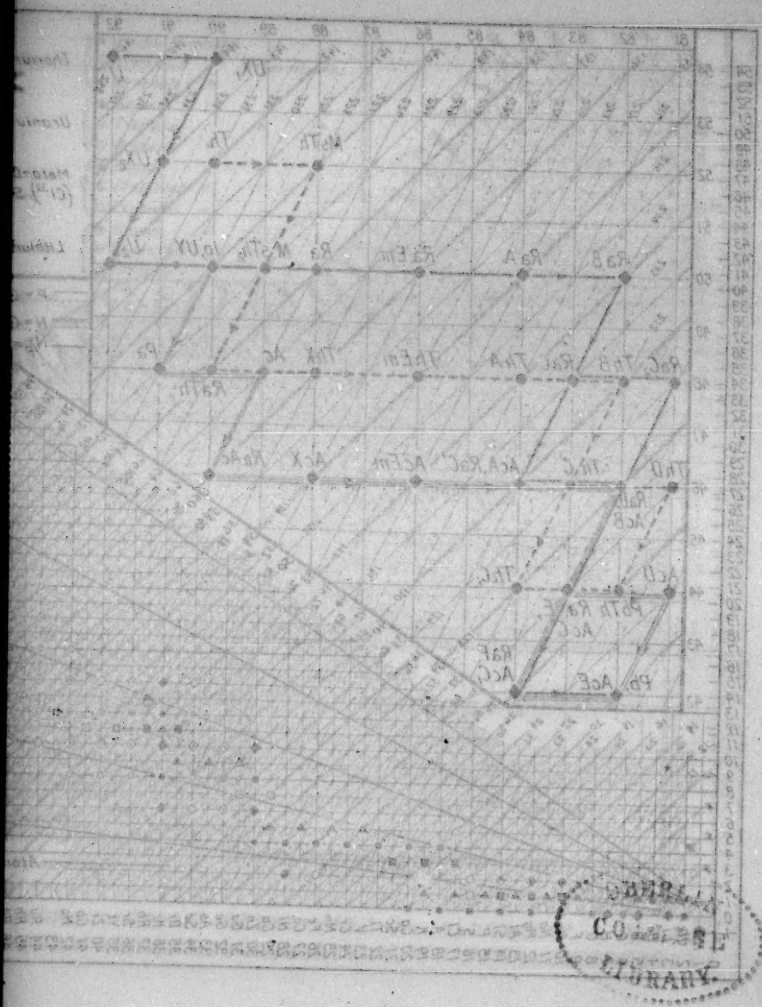
The details of the general periodic system as presented in Fig. 21, prepared for the writer by S. L. Madorsky, are of importance in the consideration of the nature of the groups present in atom nuclei. This figure plots every possible value, within the limits so far discovered, of the atomic number (X-axis), isotopic number (Y-axis), number of negative electrons (lines of slope −1) and number of positive elec-

TABLE XXIX B.

Distribution of Momentum in the Disintegration of Atoms by α-Particles.

Element.	H-particle		Residual Nucleus		α-particle.	Per cent. Gain in Energy.
	Forward.	Backward.	Forward.	Backward.		
Boron	2.02 *V*	−1.75 *V*	−0.54 *V*	3.23 *V*	2.52 *V*	42
Nitrogen	1.78 *V*	−1.32 *V*	1.44 *V*	4.54 *V*	0.78 *V*	−13
Fluorine	2.10 *V*	−1.89 *V*	−0.10 *V*	3.89 *V*	2.00 *V*	35
Sodium	2.02 *V*	−1.72 *V*	1.42 *V*	5.16 *V*	0.56 *V*	6
Aluminium	2.34 *V*	−2.11 *V*	0.78 *V*	5.23 *V*	0.88 *V*	42
Phosphorus	2.10 *V*	−1.89 *V*	1.14 *V*	5.13 *V*	0.76 *V*	15

trons (lines of slope −2). *Every corner where all of these 4 lines meet represents a possible isotope.* This plot is of interest in that it shows very well that atomic species are found only in a relatively narrow band of the general form of a parabola. The equation of the parabola has been calculated by Professor A. C. Lunn from entirely general considerations, without paying attention to the specific data given here. The lines radiating from the origin give the values of the relative negativeness (N/P) of the nuclei. Fig. 12, already presented, represents a limited portion of the same diagram, and gives a better idea of the periodicity with respect to the atomic and isotopic numbers than the present figure, since in the latter the periodicity is obscured by the abundance of detail. However, Fig. 21 shows the periodicity with respect to the number of positive and negative electrons, which requires a very large plot for complete representation. Even numbers of negative electrons are represented by double, and odd numbers by single, lines. Of the approximately 70 atomic species, in the non-



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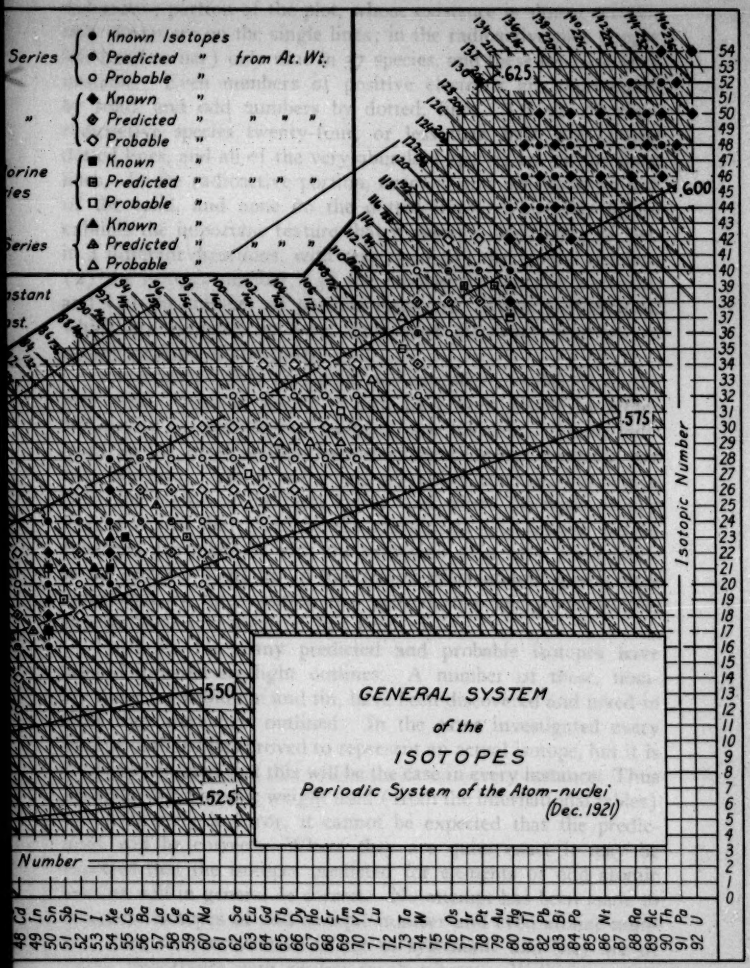
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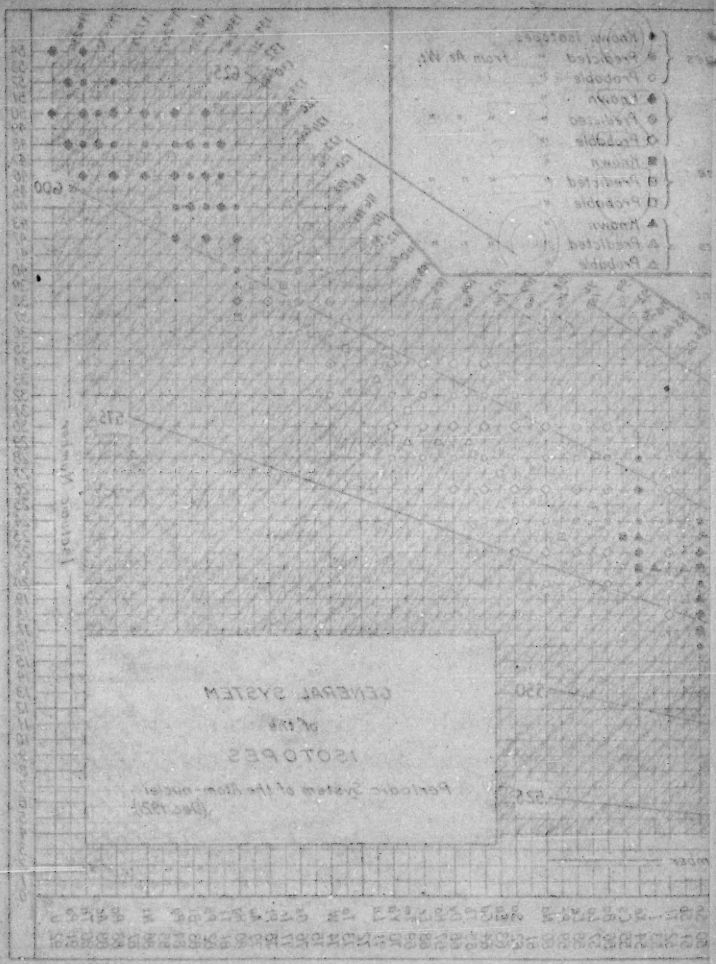

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radioactive portion of the plot, whose existence is almost certain, only eleven are on the single lines; in the radioactive plot (upper left-hand corner) only nine in 37 species, and these nine are very unstable. Even numbers of positive electrons are represented by solid, and odd numbers by dotted, lines. Of the 70 non-radioactive species twenty-four, or less than half, are on the dotted lines, and all of the very abundant species are on the solid lines. In the radioactive portion, every atomic species is on one of the solid, and none on the dotted lines. Thus this figure exhibits the important feature that it shows a periodicity of two in 4 different directions, with respect to (1) the atomic number, (2) the isotopic number, (3) the number of negative electrons, and (4) the number of positive electrons. These periodicities, which are summed up here, have been discussed in detail in earlier sections of the paper.

The symbols used are, with one exception, explained in the plot itself. Atomic species, which have been found by either radioactive or positive-ray methods, are inked-in. Those indicated by the latter method, whose existence seems doubtful, are half inked-in. Those not found by either method, but which lie in the region of the light atoms, and where the mean atomic weight is just that given by the Harkins-Wilson atomic weight equation, are inked-in with the exception of a very small circle in the centre. Thus far in this region every atomic species thus designated by the equation has proved to exist, whenever the experimental investigation has been made.

Positions for many predicted and probable isotopes have been designated by light outlines. A number of these, notably those for rubidium and tin, have been discovered and inked-in since they were first outlined. In the cases investigated every isotope outlined has proved to represent an actual isotope, but it is not to be expected that this will be the case in every instance. Thus when the mean atomic weight used (from the international tables) is considerably in error, it cannot be expected that the predictions will be correct. Where they are quite exact it may be expected that the isotopes predicted for elements of odd atomic number will in general be correct. No attempt has been made to designate isotopes of odd isotopic number and even atomic number, since their occurrence is not so systematic and they are of minor importance with respect to abundance. With increasing

sensitiveness of the positive-ray method, it may be expected that more isotopes of this class will be discovered, and the same may be true of the species of odd atomic and even isotopic number, which are extremely rare.

43. CLASSIFICATION OF THE ATOMIC SPECIES BY SERIES.

The classification of all atomic species into 4 series, each of which naturally forms 2 classes, a principal and a secondary series, was suggested by the writer several years ago.[46] The classification is presented in Table XXX. In each case A is the principal, and B is the subordinate, series.

The relationship between the series of Table XXX and of the classes of isotopes according to section 33 is exhibited in Table XXXI.

44. HYPOTHESES IN REGARD TO THE STRUCTURE OF COMPLEX ATOM NUCLEI.

Thus far the present paper has been concerned with facts and their obvious interpretation. The subject of the structure of a complex nucleus introduces considerations of a more hypothetical nature. The model of the alpha particle already presented (Fig. 3, Section 23) represents a particle which, while it has a net charge of 2 positive, is nevertheless largely electrically negative in its exterior. Such particles, since they contain both positive and negative electrons which are not coincident in space, may act as electrical couples, and thus attract each other sufficiently to unite to form a vary stable nucleus of greater mass. In this way 3, 4, 5, 6, 7, 8, 9, or 10, but *not* 2 alone, form sufficiently stable complexes to give rise to atomic species of considerable abundance. The fact that 2 α-particles do not seem to make a stable structure, suggests that a ring or shell structure[47] of the alpha particles may be essential for stability. Thus the beryllium nucleus, if it were built up exactly according to the numerical system with respect to α-particles as holds for the other atoms of even atomic number, should consist of two α-particles (α_2), but actually its atomic weight corresponds to $\alpha_2\eta\beta$. Thus either an additional α-particle, or the group $\eta\beta$ seem

[46] *Nature* (April, 1920), and in more detail in *J. Am. Chem. Soc.*, **42**, p. 1958 (1920).

[47] Harkins: *Physical Review*, **15**, 82 (postulate 12) (1920).

TABLE XXX.

Classification of the Atomic Species into Series.

q, a, and b, represent *any* whole numbers. E = Even No., M = At. No., n = Isotopic No.

I Thorium (Helium-Thorium) $P = 4q$		II Uranium (Metaneon-Uranium) $P = 4q+2$		III Lithium (Li-Co-I-) $P = 4q+3$		IV (Be-Cl^{37}_{3}-Xe^{131}_{54}-Cs) $P = 4q+1$	
A $M = E$ $n = 4q$	B $M = O$ $n = 2q$ (not $4q$) $n = 4q+2$	A $M = E$ $n = 2q$ (not $4q$) $n = 4q+2$	B $M = O$ $n = 4q$	A $M = O$ $n = 4q+1$	B $M = E$ $n = 4q+3$	A $M = O$ $n = 4q+3$	B $M = E$ $n = 4q+1$
$\alpha_a\beta_{2b}$	$\alpha_a\beta_{2b}\beta$	$\alpha_a\beta_{4b}\alpha_1\beta^2$	$\alpha_a\beta_{2b}\gamma_1\beta_1\beta$	$\alpha_a\beta_{2b}\gamma_1\beta_2$	$\alpha_a\beta_{2b}\gamma_1\beta_1\beta$	$\alpha_a\beta_{2b}\gamma\beta\beta$	$\alpha_a\beta_{2b}\alpha\beta\beta_2$
He_0^4			Li_0^6	Li_1^7			Be_1^9
$C6^{12}$			$B5_0^{10}$	$B5_1^{11}$			
$O8_0$			$N7_0^{14}$	$F9_1^{19}$			
$Ne10_0^{20}$		$Ne10_1^{22}$		$Na11_1^{23}$			$Ne10_1^{21}$ (?)
$Mg12_0^{24}$		$Mg12_2^{26}$		$Al13_1^{27}$			$Mg12_1^{25}$
$Si14_0^{28}$		$Si14_2^{30}$ (?)		$P15_1^{31}$			$Si14_1^{29}$
$S16_0^{32}$				$Cl17_1^{35}$		$Cl17_0^{37}$	
$A18_0^{36}$				$K19_1^{39}$		$K19_0^{41}$	
$A18_4^{40}$						$Sc21_0^{45}$	
$Ca20_0^{40}$							
$Ca20_4^{44}$							
$Ti22^{48}$							
$Cr24_4^{52}$				$V23_0^{51}$			
$Fe26_4^{56}$				$Mn25_0^{55}$			
$Ni28_4^{60}$		$Ni28_2^{58}$		$Co27_0^{59}$			
$Zn30_4^{64}$		$Zn30_0^{64}$					
$Zn30_6^{68}$		$Zn30_{10}^{70}$					
$Kr36_0^{80}$		$Kr36_4^{78}$		$As33_0^{75}$			
$Kr36_{12}^{84}$		$Kr36_{10}^{82}$ $Kr36_{14}^{86}$		$Br35_0^{79}$	$Kr36_{11}^{83}$	$B\ 35_{11}^{81}$	
$Sn50_{18}^{116}$		$Sn50_{18}^{118}$		$Rb37_{12}^{87}$		$Rb37_{11}^{85}$	$Sn50_{17}^{117}$
$Sn50_{20}^{120}$		$Sn50_{22}^{122}$			$Sn50_{19}^{119}$		$Sn50_{21}^{121}$ (?)
$Sn50_{24}^{124}$				$I53_{21}^{127}$			$Xe54_{21}^{129}$
$Xe54_{20}^{128}$		$Xe54_{22}^{126}$					
$Xe54_{24}^{132}$		$Xe54_{26}^{134}$			$Xe54_{23}^{131}$		
$Xe54_{28}^{136}$						$Cs55_{23}^{133}$	
$Hg80_{40}^{200}$		$Hg80_{38}^{198}$ (?)			$Hg80_{39}^{199}$ (?)		$Hg80_{37}^{197}$ (?)
$Hg80_{44}^{204}$		$Hg80_{42}^{202}$					

TABLE XXX—*Continued.*

2. Radioactive Atomic Species.

I Thorium (Helium-Thorium) $P = 4q$		II Uranium (Metaneon-Uranium) $P = 4q+2$		III Lithium (Li-Co-I-) $P = 4q+3$		IV (Be-Cl_3^{37}-Xe_{17}^{121}-Cs) $P = 4q+1$	
A	B	A	B	A	B	A	B
$Pb82_{44}^{208}$	$Tl81_{48}^{208}$ (ThD)	$Pb82_{42}^{206}$	$Tl81_{48}^{210}$ (RaC_2)				
		$Pb82_{46}^{210}$ (RaD)	$Bi83_{44}^{210}$ (RaE)				
$Pb82_{48}^{212}$ (ThB)	$Bi83_{46}^{212}$ (ThC)	$Pb82_{50}^{214}$ (RaB)	$Bi83_{48}^{214}$ (RaC)				
$Po84_{44}^{212}$ (ThC_1)							
$Po84_{46}^{216}$ (ThA)		$Po84_{48}^{214}$ (RaC^1)					
$Nt86_{48}^{220}$ (ThEm)	$Ac89_{50}^{228}$ ($MsTh_2$)	$Po84_{50}^{218}$					
$Ra88_{48}^{224}$ (ThX)		$Nt86_{50}^{222}$ (RaEm)					
$Ra88_{52}^{228}$ (MsTh)		$Ra88_{50}^{226}$ (Ra)	$Pa91_{52}^{144}$				
$Th90_{48}^{228}$ (RaTh)		$Th90_{50}^{230}$ (Io)					
$Th90_{52}^{232}$ (Th)		$Th90_{54}^{234}$					
		$U92_{50}^{234}$ (UII)					
		$U92_{54}^{238}$ (U)					

TABLE XXXI.

Relationship between the Classes and Series of Atomic Species.

	Class I	II	III	IV
Series	Thorium A Uranium A	Lithium A Meta-chlorine A	Thorium B Uranium B	Lithium B Meta-chlorine B

to be essential to cement two α-particles together. It may be seen, however, that the evidence is not at all conclusive with respect to a ring structure, since the third particle or group may be needed merely to increase the attraction. Thus a few molecules will not form a stable raindrop, since the vapor pressure is too high, but the escaping tendency of the molecules decreases rapidly as the number of molecules increases.

When the number of α-particles increases above 10, the value of the relative negativeness (N/P) of the nucleus is too small

(0.5) to keep it stable. The simplest way in which such a nucleus may be stabilized is by the addition of two extra electrons, which would be much less firmly bound than those present in the α-particles themselves. The latter may be termed "binding electrons," while the former, one pair of which serves to attach one extra α-particle to the nucleus, may be styled "cementing electrons." In the α-disintegrations of radioactive atoms cementing, but no binding, electrons are given off. For example, the nucleus of the more stable isotope of argon (A_4^{40}) may be considered as $a_9{+}{+}(a{+}{+}e^-e^-)$. The group (aee), which is electrically neutral, has been designated by the writer as a "helio" group, since it has the composition, but not the structure, of a complete helium atom. The α-particle of the helio group is sometimes designated as an a' group. It will be seen that this group adds 4 to the atomic weight, and nothing to the nuclear charge or atomic number, so it is a quadruple neutron. In radioactive disintegrations the group is not emitted as a unit, but as a single α and two separate β-particles. In A_0^{36} the value of N/P is 0.500, but the addition of a helio group raises this ratio to 0.550. Proceeding from the lowest atomic numbers, argon of atomic number 18, is the first which adds on one helio group (two cementing electrons) while $Zn30_8^{68}$ is the first species to contain two helio groups (4 cementing electrons). $Kr36_{12}^{84}$ has the lowest atomic number of any species yet discovered in which the number of helio groups is 3 (6 cementing electrons), though it is probable that there is a corresponding isotope of selenium, and possibly of germanium.

The energy of formation of an α-particle from 4 protons and 2 electrons is 4.63×10^{-5} erg, a very great amount of energy when the mass involved (6.60×10^{-24} g.) is taken into account. The kinetic energy of the fastest α-particles given off in radioactive disintegrations has almost one-half as high a value as the energy of formation of the particle. Thus the energy of an α-particle from thorium-C is about 2.2×10^{-5}, while that from radium-C is about 1.2×10^{-5} erg. While the kinetic energy of such particles would not seem to be sufficient to break up an alpha particle, it would seem that it should be sufficient to disrupt some of the α-particles from more complex nuclei; particularly since the fact that atomic species whose nuclei which are complexes of

α-particles exhibit practically the same packing effect as helium itself, so that the total energy of combination of the alpha particles must be relatively small. *The greatest uncertainty in the packing effect in the union of alpha particles lies at present in the atomic weight of helium,* though this has not always been recognized in some of the recent discussions of this topic.

45. GROUPS INVOLVED IN THE DISINTEGRATION OF RADIOACTIVE ATOMIC SPECIES.

In the last section it was assumed that some of the α-particles in complex nuclei are attached by two negative electrons. Thus they contain α-particles which are converted into *neutral groups* (helio groups), and other α-particles which are not thus neutralized. In thorium there are 12 neutral to 45 non-neutral alpha particles $[45\alpha^{++} + 13(\alpha\beta\beta)^{\circ}]$.

Hypothesis 1.—Thorium disintegrates with a half-period of 1.5×10^{10} years giving off an alpha particle to form mesothorium 1, which may be

$$44\alpha^{++} + 13(\alpha\beta\beta),$$

which in turn gives off a β-particle with a period of 6.7 years, and forms

$$44\alpha^{++} + 12(\alpha\beta\beta) + (\alpha\beta)^{+}.$$

This contains a cementing electron which is not present in a neutral part, so it gives off the odd electron very quickly, with a half-period of 6.2 hours, to form

$$44\alpha^{++} + 12(\alpha\beta\beta).$$

This gives an α-disintegration with a half-period of 1.9 years. After this three more α-changes follow with constantly decreasing periods, the last half-period being 0.14 seconds. *These facts gave rise to the hypothesis*[48] *that both the alpha and the beta particles are in groups, the latter in groups of 2 and the former in groups of 1 to 10, but usually of about 4. When a group is once broken it becomes less and less stable as it becomes smaller.* (Consult the average life of radioactive atoms given in Fig. 1.)

Hypothesis 2.—In the first hypothesis it was assumed that the electrons of the helio group were, in the above-mentioned changes, given off before its α-particle, which may be designated

[48] Harkins: *Physical Review,* 15, 88 (Feb., 1920).

as an α'-particle to distinguish it from other alpha particles. In the second form of the hypothesis it will be assumed that the α'-particle is given off from the neutral group before the electrons.[49]

According to this idea mesothorium 1 would be

$$45\alpha^{++} + 12(\alpha\beta\beta) + (\beta\beta).$$

This would give off a β-particle to form

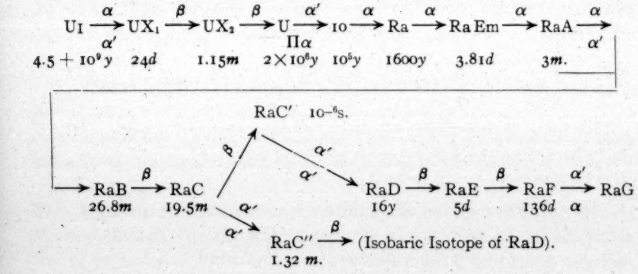
$$45\alpha^{++} + 12(\alpha\beta\beta) + \beta.$$

Since this contains a single electron not attached to any specific neutralizing group, it would readily escape, as corresponds with the low period. The two hypotheses are outlined in Table XXXII.

TABLE XXXII.

Disintegration of the Radium Series Elements According to the Two Hypotheses.

(Hypothesis 1 above, 2 below, arrows marked with an α'.)


UI α UX1 β UX2 β U α′ IO α Ra α Ra Em α RaA α
α′ Πα α′
4.5 + 10⁹y 24d 1.15m 2×10⁶y 10⁵y 1600y 3.81d 3m.
RaC′ 10⁻⁶s.
β α′
α′
RaB β RaC α′ RaD β RaE β RaF α′ RaG
26.8m 19.5m 16y 5d 136d α
α′
α′
RaC″ β (Isobaric Isotope of RaD).
1.32 m.

It will be seen that hypothesis 1 leads to a very much more consistent scheme than hypothesis 2 for the representation of the branching of the series.

[49] The general idea of the existence of these neutral helio groups was developed by the writer in 1920 (*J. Am. Chem. Soc.*, **42**, 1958–65, 1920), without any stated preference for either of the two forms of the hypothesis given above. A year later L. Meitner (*Z. f. Physik*, **4**, 146, 1921) expressed a preference for the latter of the two possibilities. Fajans discusses this question, *Radioaktivität*, pp. 90–96 (1922).

46. STRUCTURE OF NUCLEI WHOSE ATOMIC WEIGHTS ARE NOT DIVISIBLE BY 4.

In considering the structure and composition of nuclei not built up from alpha particles (a) and electrons alone, it is important to inquire what other groups than the alpha particle may be present. Table XXXIII lists the protons (p) and electrons (e) which must be present in order to account for the atomic weights and atomic numbers of atomic species of isotopic numbers 0 to 4.

TABLE XXXIII.

Formula-Groups other than Alpha Particles Necessary to Account for the Composition of Atomic Species.

Isotopic Number.	Atomic Number. Even				Odd			
	Group	Series	Class	No.†	Group	Series	Class	No.†
0	.....	ThA	I	9	p_2e	UB	IV	3
1	pe	BeB	III	3	p_2e_2	LiA	II	8
2	p_2e_2	UA	I	2	$a^{++}e^{-}$	ThB	IV	0 R*
3	p_3e_3 or ep_2e_2 (?)	LiB	III	0 Ki^{83}_{11} Sn^{119}_{19} Xe^{131}_{23}	$ap e_2$	BeA	II	3
4	ae_2	ThA	I	7	aep_2e_2	UB	IV	0 R*

* R indicates species found thus far only in radioactive disintegration series. Thus such species are extremely rare, and in general extremely unstable. Note that both types of species thus indicated belong to Class IV, and to B or subordinate series.

† The column headed "No." gives the number of atomic species of atomic numbers 1 to 28 and of isotopic numbers 1 to 5 inclusive, as shown in Fig. 12.

In considering the structural relations of the protons and electrons of these formula groups to the rest of the nucleus, it is important to keep the following facts in mind:

1. Almost all atoms contain an even number of negative electrons.

2. Most atoms contain an even number of positive electrons.

3. In atoms in which there is an odd number of negative electrons, the number of positive electrons is also almost always odd, *so there is a tendency for the positive and negative electrons to match each other in oddness or evenness.*[50] *Thus an oddness of N, when it does occur, is almost always an accompaniment of an odd value of P.*

[50] See *Phil. Mag.*, **42** (1921), paragraph 4, p. 308 and p. 320.

Since the alpha particle contains an even number of both protons and electrons, this indicates that in the other formula-groups there is a strong tendency toward the formation of *neutral groups.*

4. In the meteorites the most abundant groups other than the α-particle, are pe, p_2e_2, and p_3e_2.

5. Thus far Rutherford has obtained long-range H-particles (protons or positive electrons) only from nuclei which contain formula-groups p_2e and p_3e_2, that is *only when there are more protons than electrons in the group.* This fact does not seem to be recognized by Rutherford himself. (Section 41, and Tables XXIX and XXX).

6. When aluminium is bombarded by α-particles nearly as many long-range H-particles are emitted in the backward, as in the forward, direction of the α-particles (Section 41).

7. H-particles are not emitted from radioactive substances, so far as is now known, and long-range H-particles have not been obtained from elements of atomic number greater than 15. This may be due to the fact that the higher positive charge of the nucleus prevents the α-particle from approaching closely enough to disrupt an H-particle, but it suggests that the protons may become more or less buried by the increasing number of α-particles.

8. Atoms with formula-groups p_3e_3 are extremely rare.

Several hypotheses as to the grouping of the protons and electrons of the formula-groups are presented below.

Hypothesis 1.—All of the negative electrons in atom nuclei, other than the binding electrons of the α-particles, serve as cementing electrons for the α-particles (or else they are attached to the part of the nucleus which contains the α-particles, without taking on the function of cementing electrons).

Hypothesis 1, A.—The protons, one, two, or three in number, form a ring, which rotates around the inner or alpha portion of the nucleus. This is the hypothesis favored by Rutherford. However, he does not give any consideration to the part played by the negative electrons of the formula-groups, and this, it may be seen, is of fundamental importance. Table XXVIII gives the formula-groups pe, pe_2, p_2e, p_2e_2, and p_3e_2, which *do not exhibit* any *simple relation between the number of electrons and protons,* and this makes it seem probable that if the protons form a ring, the electrons do not enter the ring, but attach themselves to the

inner nucleus, that is, to the part built up of α-particles. These electrons would increase the relative negativeness (N/P) of the inner nucleus sufficiently to enable it to attach extra protons which form the ring. For example, in the more abundant isotopes of magnesium the nucleus contains 24 protons and 12 electrons, presumably in the form of 6 α-particles, and the value of N/P is 0.5. Now if this were to take up two electrons (possibly as cementing electrons) the value of N/P would rise to 0.583, which is higher than for any known atomic species of low atomic number. Being relatively so negative, the nucleus would add two or three protons in the form of a ring. If 2 protons, then N/P would be reduced to 0.538, and an isotope of magnesium would be formed. If 3, then N/P would be reduced to 0.519, and aluminium would be given. Both of these values of the relative negativeness correspond to a condition of stability.

The negative planetary electrons of the innermost, or K ring, seem to be held by the electrostatic attraction of the positive charge of the nucleus. In order that positive protons should be attracted, it would seem that their distance must be very much smaller, possibly within 10^{-11} cm. or less from the outer part of the inner nucleus.

Hypothesis 1, B.—The protons attach themselves to the alpha particles or negative electrons of the nucleus, but the formula-group is not associated as such. The discussion given under A would be mostly in point here.

Hypothesis 2.—Groups, other than the α-particles, which contain electrons as well as protons, are present in the nucleus. These groups need not in all cases have the composition of the formula-group, but it is not unlikely that at least a part of the groupings in the nucleus have the composition of the formula-group. Facts 3 and 5 listed above suggest that the groups p_2e and p_2e_2 may be best represented as $(pe)p$ and $(p_2e_2)p$, respectively, to indicate that the addition of a proton to the neutral groups (pe) or (p_2e_2) introduces an instability with respect to the emission of protons.

While Rutherford favors hypothesis 1, it is the opinion of the writer that hypothesis 2 is in better accord with the facts now known, since there seems to be a very marked dependence of the stability of the nucleus upon the relation between the number of

electrons and protons in the formula-group, which would be very unexpected in case they are placed entirely independently as in Rutherford's hypothesis.

It would be of interest to determine if negative electrons are driven off from Cl_3^{37}, K_3^{41}, and Sc_3^{45}, which are supposed to contain the formula-group $(pe)e$. The great rarity of atoms which contain the formula-group p_3e_3 suggests that it is not unlikely that no moderately stable actual group contains more than two electrons, unless some cementing electrons are counted in. The only species now known which contain the group in question are $Kr36_{11}^{83}$, $Sn50_{19}^{119}$, and $Xe54_{23}^{131}$. These are very rare, and have positions in the system which seem to indicate that each such nucleus contains an odd or unpaired cementing electron. This would indicate that the electron-proton group in these atoms is $(p_3e_2)e$, and that the third electron acts as a cementing electron.

47. ENERGY LIBERATED IN THE DISINTEGRATION OF THE RADIOACTIVE ATOMIC SPECIES.

The mass equivalent of the energy involved in the disintegration of the various radioactive species has already been given (Section 24, Table XV). The values were calculated from data on the ranges of the particles as given in the literature in the year 1914. The table did not include the heating effect of the β and γ-rays. Table XXX gives the latest determinations of the heating effect of the principal atomic species in the radium series as taken from the work of Rutherford.

TABLE XXXIV.

Heating Effect of the Various Rays in the Disintegration of the Atomic Species of the Radium Series.

(Gram calories per hour per g. Ra)

Atomic Species.	α	β	γ	Total.
Ra	25.1			25.1
RaEm	27.6			27.6
RaA	30.5			30.5
RaB				
RaC	39.4	4.3	6.5	50.2
	123.6	4.3	6.5	134.5

The velocity of fast β-particles corresponds to what would be given them by a potential drop of about 3 million volts, that of the α-particles to 4 million volts, and the energy of the hardest γ-rays to 3 million volts.

A magnetic analysis of the β-rays of RaB shows that they give a line, as well as a continuous spectrum. According to Rutherford, Robinson, and Rawlinson [51] the lines are due to the conversion of monochromatic γ-rays in the same radioactive atom which emits them, the strong lines being due presumably to a conversion of these rays in the K ring, and the weaker lines to conversion in the L_3 ring.[52] Ellis uses the β-ray line spectrum as a means of determining the wave-lengths of short γ-rays. The shortest wave-length measured by the crystal method is 0.07 A, but many γ-rays have shorter wave-lengths than this. The new method consists in measuring the energies of different lines of the natural β-ray spectrum of the atomic species. If a certain line corresponds to the energy E_1 and is produced by a line of frequency ν, then the following quantum relation seems to hold:

$$E_1 = h\nu + w_1$$

where w_1 is the work needed to remove the electron in question to the surface of the atom. To find the frequency, all that is necessary is to determine w_1, which may be done by measuring the energy of the corresponding line in the *excited* spectrum of a substance of adjacent atomic number. In the latter case the electron will come from a corresponding level, but the energy used in removing the electron to the surface will be w_2. The difference in the energies of the corresponding β-ray lines, $E_1 - E_2$, is obviously equal to $w_1 - w_2$, and is determined directly. To find w_1 it is only necessary to see which of the corresponding levels of the two atoms differ by this amount, which may be done from the X-ray absorption data.

When sufficiently strong radioactive sources to give excited spectra cannot be obtained, the natural β-ray spectrum is analyzed by inspection. Frequently two or more lines can be found which differ in energy by the same amount as certain known levels in the atom; for example, the K and the L levels, or the $L_3L_2L_1$ levels. Table XXXV gives the wave-lengths and voltages of the γ-rays of Th D as determined by the latter method.

According to Rutherford the γ-rays are emitted from the *nuclei* of atoms, and if this is true, important information in

[51] Rutherford, Robinson, and Rawlinson: *Phil. Mag.*, **28**, 281 (1914); Rutherford, *ibid.*, **34**, 153 (1917).

[52] Ellis: *Proc. Roy. Soc.*, **A101**, 1–17 (1922).

regard to the nucleus can be obtained from such values as those given in Table XXXV.

It is possible that the β-rays given below may come partly from Th C. The energy of these rays from Th C and D mixed has been observed as high as 8×10^5 volts.

TABLE XXXV.

Wave-lengths and Corresponding Voltages of the γ-rays of ThD (At. No. = 81) as Determined by Ellis from the β-ray Spectrum.

Number.	Energy in Volts.	Wave-length in A.
1	6.54×10^5	0.0189
2	5.11	0.0241
3	2.86	0.0431
4	2.74	0.0450
5	2.54	0.0486
6	2.48	0.0498
7	2.28	0.0541
8	2.06	0.0599
9	0.560	0.220
10	0.408	0.302

Absorption Voltages of ThD (Thallium).

Ring.	Energy in Volts.	Wave-length.
K	0.869×10^5	0.1427
L_3	0.154	0.803
L_2	0.147	0.840
L_1	0.127	0.974

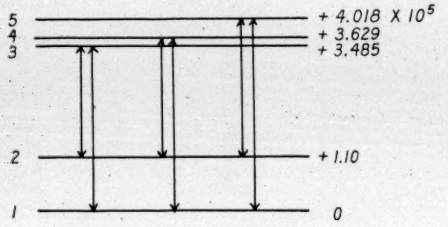
On the basis of Rutherford's hypothesis that the lines of the β-ray spectrum are due to a conversion of the monochromatic γ-rays in the same atom which emits the latter, Ellis concludes that the γ-rays are emitted previous to the actual disintegration of the nucleus; since Rutherford and Andrade found that Ra B, a form of lead, gives the complete K and L spectrum of lead (At. No. = 82). The principal γ-rays of Ra B correspond to energies of 2.4 to 4.0×10^5 volts, and must therefore come from within the K ring of planetary electrons. Chadwick [53] investigated the field of force in the region of the atom between the K ring and the nucleus and concluded, in accordance with the general previous opinion, that no electrons are present. If this is true, the γ-rays must come from the nucleus, as accords with Rutherford's idea.

If the γ-rays from Ra B are emitted previous to the disintegration, then, Ellis concludes, it should be possible to deduce information in regard to this nucleus from them. It is found that

[53] Chadwick: *Phil. Mag.*, **40**, 734 (1920).

there is a simple arithmetical connection between the energies of the γ-rays, the first three energies being, respectively, 1.1×10^5 greater than the last three. This suggests that quantum dynamics may be used in connection with the nucleus, and indicates the five levels of Fig. 22 for the Ra B nucleus. As a consequence of the existence of these levels there should also be γ-rays corresponding to transitions from 5 to 4, 5 to 3, 4 to 3, and 2 to 1.

FIG. 22.



Energy levels in the nucleus of atoms of radium-B (Ellis).

Gamma rays corresponding to these energy differences were measured by the crystal method by Rutherford and Andrade, and the agreement between the observed and calculated values may be seen in Table XXXVI.

TABLE XXXVI.

Application of the Quantum Relation to the γ-Ray Spectrum of Ra B. (Ellis.)

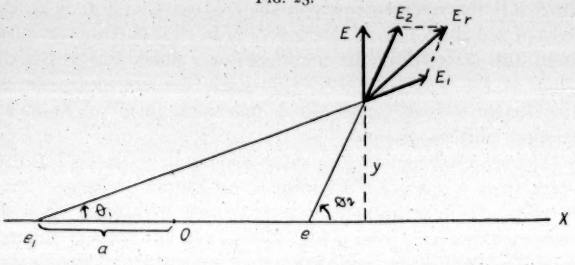
Origin.	Energy in Volts.	Wave-length in A	
		Calculated.	Observed.
5 – 4	0.389×10^5	0.318	0.324
5 – 3	0.533	0.231	0.229
4 – 3	0.144	0.857	0.853
2 – 1	1.10	0.112	0.115

It is, of course, possible that the spectrum may be emitted, not prior to, but during, the disintegration, when the change in the stationary states in the nucleus would not occur in the nucleus of a single atomic species, but in the change from one species to another. However, it seems probable that the data indicate that in the nucleus there is a fall of an electron, an alpha particle, or possibly, but not very probably, a proton, from one energy level to another.

48. CALCULATION OF THE MUTUAL ELECTROMAGNETIC MASS OF A SIMPLE SYSTEM BY PROFESSOR A. C. LUNN.

In the years 1914 and 1915, when the theory presented in the present paper was first developed, the idea was adopted that the packing effect of 0.77 per cent. involved in the change between hydrogen, on the one hand, and helium or other complex atoms, on the other, is due to a negative mutual electromagnetic mass. A general discussion of this effect has been given in Section 7 of the present paper. It seemed important to obtain a calculation which would show whether the magnitude of the loss of electromagnetic mass due to the approach of protons to electrons, could be of such

FIG. 23.



a considerable magnitude as this. The problem was first attacked by E. D. Wilson, who was working with the writer, but the assistance given him by Professor Lunn amounted actually to the solution of the problem by the latter, as given below.

Let **E** be the vector of electrical intensity (Fig. 23),
H the vector of magnetic intensity,
G the electromagnetic moment,
c the velocity of light,
u the velocity of the system.

The problem thus presented for solution is the determination of the sign and the magnitude of the change of mass which results when a positive and a negative electron are brought extremely close together.

Lorentz [54] speaks of this problem, but does not solve it either

[54] H. A. Lorentz: "The Theory of Electrons," 1909, pp. 47 and 48. In a conversation with the writer Lorentz stated that the idea had not occurred to him of explaining the deviations of the atomic weights on the hydrogen basis from whole numbers, in this way.

with respect to the sign or the magnitude of the effect. He does state, however, that if the electrons were to be brought into immediate contact, the total energy could not be found by addition, which may be considered as equivalent to the statement that the mass of a system made up in this way would not be the same as the sum of the masses of its parts. The fundamental equations used here as the basis of the calculation which follows have been taken from the work of Lorentz.

The value of e, the charge on the electron, may be defined as

$$e = \iiint \rho dr,$$

where ρ is the volume density of the electricity, and dr is an element of volume. For the purposes of the first part of the calculation, the electron may be considered as a point charge, but the values of the electromagnetic mass used later are given for the Lorentz form of electron, which takes the form of an oblate spheroid when in motion.

The space surrounding an electron must be considered as different from a space not adjacent to an electrical charge. If a charged particle is brought into this space it is acted upon by a force which varies from point to point, and has at every point in space a definite value and direction. This force is designated by **E**, and is a vector point function. If the electron is in motion it acts as an electric current equal to eu, where u represents its velocity. The magnetic force to this motion is easily seen to be a function of the current equivalent of the moving electron, and is also a vector, designated by **H**. Then

$$\mathbf{H} = f(\mathbf{E}, u, \phi)$$

where ϕ is the angle between **E** and the direction of motion. The direction of **H** is perpendicular to the direction of u and is at the same time circular.

It is evident that the total energy of the system is a function of both the electric and the magnetic intensities. For the purposes of this calculation the mass of a system is considered as electromagnetic, and hence as a function of the energy of the system. Therefore it is necessary to use some function of both **E** and **H**. This function is designated by **G** and is called the electromagnetic momentum.

For a field which is determined by a system of charges, the value of **G** is given as

$$\mathbf{G} = \frac{[\mathbf{EH}]}{c} = \frac{[(\Sigma_i \mathbf{E}_i)(\Sigma_j \mathbf{H}_j)]}{c} = \frac{\Sigma_i [\mathbf{E}_i \mathbf{H}_i]}{c} + \frac{\Sigma_{(ij)} [\mathbf{E}_i \mathbf{H}_j]}{c}$$

where the sum $\Sigma_{(ij)}$ is the vector product of every i with every j. The first summation gives the value of **G** which would belong to the particles provided their fields do not overlap, and the second expression which is of importance here, exhibits the effects of overlapping fields. This may be called "the mutual electromagnetic momentum." This may be designated by $\overline{\mathbf{G}}$.

For point charges

$$\mathbf{E}_1 = \frac{(1 - u^2)e_1}{4\pi r^2 (1 - u_1^2 \sin \Theta_1)^{3/2}}$$

at the point $P(x\,y\,z)$. Let

$$1 - u^2 \sin^2 \Theta_1 = \beta_1^2 \text{ and } (1 - u^2) = k^2.$$

The transverse component of **E** due to the two particles 1 and 2 is

$$\mathbf{E}_t = \frac{k^2 e}{4\pi} \left\{ \frac{\sin \Theta_1}{r_1^2 \beta_1^3} \pm \frac{\sin \Theta_2}{r_2^2 \beta_2^3} \right\}$$

where the sign is *positive* if the charges have the same sign, and *negative* if they are of opposite sign. As only the longitudinal component of the vector **G** is desired, only the transverse component of **E** is needed.

$$\mathbf{H} = \frac{u}{c} \mathbf{E} \sin \phi$$

where ϕ = angle between **E** and the direction of u. If $\mathbf{E}_t$ is used $\phi = 90°$. Therefore

$$H = \frac{u}{c} (E_1 \sin \Theta_1 \pm E_2 \sin \Theta_2)$$

$$G_L = \frac{[E_t H]}{c} = \frac{u}{c} (E_1 \sin \Theta_1 \pm E_2 \sin \Theta_2)^2$$

and

$$\overline{G} = \pm \frac{2u}{c^2} \int E_1 E_2 \sin \Theta_1 \sin \Theta_2 \, d\tau$$

$$= \pm \frac{2u}{c^2} \frac{k^4 e^2}{(4\pi)^2} \int \frac{\sin \Theta_1 \sin \Theta_2}{r_1^2 r_2^2 \beta_1^2 \beta_2^3} d\tau$$

$$d\tau = 2\,\pi\, y\, d\, y\, d\, x$$

$$\sin \Theta_1 = \frac{y}{r_1} \qquad r_1^2 = (a+x)^2 + y^2 \qquad r_2^2 = (x-a)^2 + y^2$$

$$\beta_1^2 = 1 - u^2 \left(\frac{y}{r_1}\right)^2 = \frac{r_1^2 - u^2 y^2}{r_1^2}$$

$$r_1^2 \beta_1^2 = r_1^2 - u^2 y^2 \text{ and } r_1 \beta_1 = (r_1^2 - u^2 y^2)^{1/2}.$$

Thus

$$\bar{G} = \pm \frac{2u}{c^2} \frac{k^4 e^2}{(4\pi)^2} \int_0^{\infty} dx \int_{-\infty}^{+\infty} dy \frac{2\pi y^3}{(r_1\beta_1 r_2\beta_2)^3}$$

$$= \pm \frac{uk^4e^2}{8\pi^3c^2} 2(2\pi) \int_0^{\infty} dx \int_0^{\infty} dy \frac{y^3}{\{[(x+a)^2+(1-u^2)y^2][(x-a)^2+(1-u^2)y^2]\}^{\frac{1}{2}}}$$

If

$$(x+a)^2 = \alpha = x^2 + 2ax + a^2$$
$$(x-a)^2 = \beta = x^2 - 2ax + a^2$$
$$\alpha - \beta = 4ax$$
$$y^4 = z \quad y^4 = z^2 \quad 4y^3dy = 2zdz$$

then

$$\bar{G} = \pm \frac{uk^4e^2}{2\pi c^2} J,$$

where

$$J = \int_0^{\infty} dx \int_0^{\infty} \frac{y^3dy}{\{[\alpha+k^2y^2][\beta+k^2y^2]\}^{\frac{1}{2}}} = \frac{1}{2}\int_0^{\infty} dx \int_0^{\infty} \frac{zdz}{\{[a+k^2z][\beta+k^2z]\}^{\frac{1}{2}}}$$

$$= \frac{1}{2}\int_0^{\infty} dx \int_0^{\infty} \frac{zdz}{[\alpha\beta + (\alpha+\beta)k^2z + k^4z^2]^{\frac{1}{2}}}$$

$$= \frac{1}{2}\int_0^{\infty} dx \left[\frac{2(\alpha+\beta)k^2z + 4\alpha\beta}{(\alpha-\beta)^2k^4\sqrt{\alpha\beta + (\alpha+\beta)kz + k^4z^2}}\right]_0^{\infty}$$

$$= \frac{1}{2}\int_0^{\infty} dx \left[\frac{2(\alpha+\beta)k^2}{(\alpha-\beta)^2k^4k^2} - \frac{4\alpha\beta}{(\alpha-\beta)^2k^4\sqrt{\alpha\beta}}\right]$$

$$= \frac{1}{2}\int_0^{\infty} dx \left[\frac{2}{(\alpha-\beta)^2k^4}\right]\left[\alpha+\beta-2\sqrt{\alpha\beta}\right]$$

$$= \frac{1}{k^4}\int_0^{\infty}\left(\frac{\sqrt{\alpha}-\sqrt{\beta}}{\alpha-\beta}\right)^2 dx + \frac{1}{k^4}\int_0^{\infty} \frac{dx}{(\sqrt{\alpha}+\sqrt{\beta})^2}.$$

If

$$x < a \quad \sqrt{\beta} = \alpha - x. \quad If\ x > \alpha, \quad \sqrt{\beta} = x - a$$

then

$$J = \frac{1}{k^4}\left[\int_0^a \frac{dx}{[(x+a)+(x-a)]^2} + \int_a^{\infty} \frac{dx}{[(x+a)+(x+a)]^2}\right]$$

$$= \frac{1}{k^4}\left[\int_0^a \frac{dx}{4a^2} + \int_a^{\infty} \frac{dx}{4x^2}\right]$$

$$= \frac{1}{4k^4}\left\{\frac{1}{a^2}\left[x\right]_0^a + \left[-\frac{1}{x}\right]_a^{\infty}\right\}$$

$$= \frac{1}{4k^4}\left\{\frac{1}{a} + \frac{1}{a}\right\}$$

$$= \frac{1}{2ak^4}.$$

Accordingly

$$\overline{G} = \pm \frac{uk^4e^2}{2\pi c^2} \frac{1}{2ak^4}$$
$$= \pm \frac{ue^2}{4ac^2\pi}.$$

The mass represented by this value of $\overline{G}$ is

$$\triangle m = \pm \frac{e^2}{4\pi c^2 a}. \quad (1)$$

Now the longitudinal mass m_1 is

$$m_1 = \frac{e^2}{6\,c^2R} \quad (2)$$

where R is the radius of the electron.

By division of (1) by (2)

$$\frac{\triangle m}{m} = \frac{3R}{d} \quad (3)$$

Equation 1 gives the effect of electromagnetic mass, which appears as a "packing effect" equal to 0.77 per cent. of the total mass. For a discussion of this effect reference should be made to Section 7.[55]

Expressed in ordinary units, the above equations become:

$$\triangle m = \frac{2e^2}{c^2 d} \quad (1)$$

and

$$m = \frac{2e^2}{3c^2R} \quad (2)$$

The total mass of a proton and an electron is

$$m_{pe} = \frac{2}{3c^2}\left\{\frac{e^2}{R} + \frac{e^2}{r} - \frac{3e^2}{d}\right\}$$

This equation was derived independently by Nicholson, but he did not apply it to explain the packing effect.[56]

49. ON THE EXISTENCE OF ALPHA PARTICLES IN COMPLEX NUCLEI.

The evidence given in the present paper shows conclusively either (1) that the nuclei of complex atoms *contain* α-particles, or that if they do not contain them they certainly (2) have been built from α-particles, and on the whole favor the idea that both of these are true. The fact, first pointed out by the writer in 1915, that the heavier atoms exhibit practically the same packing effect (0.76 per cent.) as the helium atoms, and Rutherford's experiment as well, seem to be very strongly in favor of the view

[55] By a typographical error equation 1 is given incorrectly in this section.

[56] Presented in a paper to the Physical Society, Feb. 26, 1915.

that α-particles are actually present. Brosslera [57] favors the idea that the mean packing is equal to that of the α-particle, but that the arrangement of electrons and protons is not the same as it is in such particles. Evidently, however, he is not familiar with much of the evidence presented here.

50. THE NUCLEAR AND NON-NUCLEAR PROPERTIES OF ATOMS EXHIBIT PERIODICITIES WHICH ARE ENTIRELY DIFFERENT.

According to the current view the nucleus is very minute in comparison with the space occupied by the non-nuclear system of negative electrons. In agreement with this idea, the characteristics of the nucleus have been found to be independent of the non-nuclear system. One of the best evidences that this is true is found in a comparison of the ordinary, or Mendelejeff periodic system of the elements (Fig. 24 presents one of its latest forms), which relates to the system of planetary electrons, with that of the atomic species developed by the writer, and described in the present paper (Fig. 21, and Figs. 8, 9, and 10). The two sets of figures show no resemblance in the periodicities which they exhibit. Table XXXVII shows that the periods in the chemical system are 2, 8, 18, or 32 elements in length.

TABLE XXXVII.

Periodicity of the Physical and Chemical Properties of the Elements (Planetary System of Electrons.)

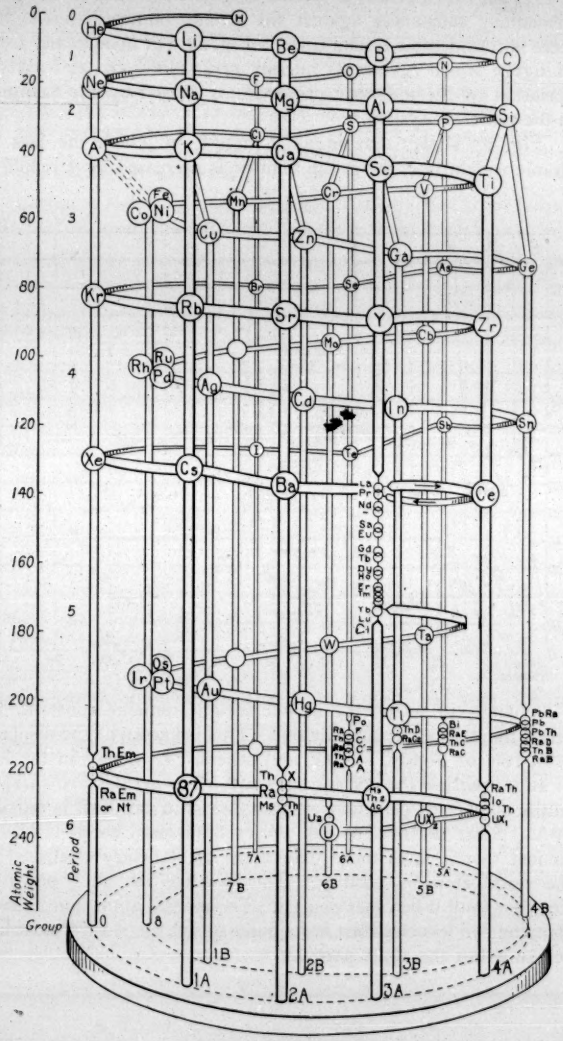
	Cycle 1.	
Period 1.	First very short period ..... H–He	$= 2 = 2 \times 1^3$ elements.
	Cycle $2 = 4^3$ elements.	
Period 2.	First short period ..... Li–Ne	$= 8 = 2 \times 2^3$ elements.
Period 3.	Second short period ..... Na–A	$= 8 = 2 \times 2^3$ elements.
	Cycle $3 = 6^3$ elements.	
Period 4.	First long period ..... K–Kr	$= 18 = 2 \times 3^3$ elements.
Period 5.	Second long period ..... Rb–Xe	$= 18 = 2 \times 3^3$ elements.
	Cycle 4.	
Period 6.	First very long period ..... Cs–Nt	$= 32 = 2 \times 4^3$ elements.
Period 7.	..... Eka–Cs–U	incomplete.

Fig. 25 shows the same periodicity in some of the physical properties; compressibilities, atomic volumes, coefficients of expansion, and melting points—when plotted against the atomic number. All of these relate to the planetary system of electrons.

A number of physicists have recently ascribed the magnetic characteristics of substances to the nuclei of atoms, but a glance

[57] *Rev. Chim.*, 1, 42, 74 (1921).

FIG. 24.

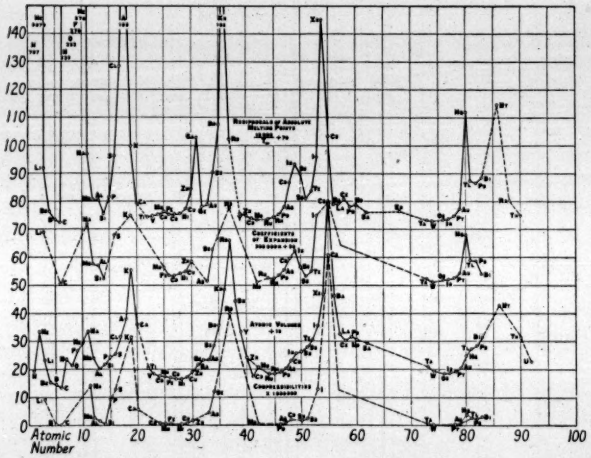


Periodic table by W. D. Harkins.

at Fig. 26, which plots the specific magnetic susceptibilities of the elementary substances against the atomic number, shows that there is considerable resemblance to Fig. 24, but none to any form of figure which represents nuclear *periodicities*, so at least the variation of the magnetic properties is caused by the variation in the planetary system.

Fig. 27 shows that in an α-change, in which the loss of atomic weight is 4, the group number is decreased by 2; while in

FIG. 25.



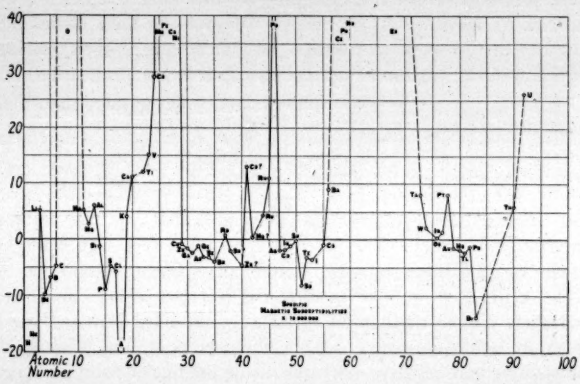
a β-change, in which the atomic weight remains constant, the group number is increased by one. This is known as the displacement rule of Soddy, Fajans, and others. Evidently in the loss of an α^{++}-particle the nucleus loses two of its net positive charges, so the number of planetary electrons which it can hold is reduced by 2. Since the nucleus has a very high-speed recoil it travels so fast that it loses more than 2 of its planetary electrons, so the recoil atom is positive. This positive ion then picks up electrons until it becomes neutral. The neutral atom thus formed contains two less electrons in its outer or valence shell, than it had before it lost the alpha particle.

In a β^--change the nucleus loses a negative charge, which means a gain of one in its net positive charge. As a result the nucleus can hold one more negative electron in the neutral atom, so one outer or valence electron is picked up.

51. SLIGHT DIFFERENCES IN THE SPECTRA OF ISOTOPES, WHICH INDICATE: (1) MINUTE DIFFERENCES IN THEIR CHEMICAL PROPERTIES, AND (2) THAT EITHER THE NON-COINCIDENCE IN SPACE OF THE CHARGES OF THE NUCLEUS, OR ITS MASS, GIVE RISE TO A FORCE WHICH ACTS ON THE PLANETARY ELECTRONS.

Ordinary lead of atomic weight 207.20, and lead from radium (Ra G), of atomic weight 206.318, have been found to exhibit

FIG. 26.



a difference of 0.0044 A. in the line $\lambda 4058$. This amounts to slightly more than one-millionth or 0.0001 per cent. of the total wave-length.[58] The discovery of this shift is of particular interest, since at least 7 careful experimental investigations made previously had led to the conclusion that the spectra of isotopes are identical.

[58] Harkins and Aronberg, *Proc. Nat. Acad. Sci.*, **3**, 710–15 (1917); Aronberg, *Astrophys. J.*, **47**, 96–103 (1918); Harkins and Aronberg, *J. Am. Chem. Soc.*, **42**, 1328–1335 (1920). The spectroscopic work was done by Aronberg, and its success was due largely to the suggestions of Professor H. G. Gale. The shift has been confirmed, both with respect to its magnitude and direction, by Merton [*Proc. Roy. Soc. of London*, **96A**, 388–95 (1920)]. The radium-lead was supplied by Professor T. W. Richards.

These investigations were as follows: Those of Russell and Rossi,[59] and of Exner and Haschek,[60] using thorium and ionium; that of Aston[61] on the isotopes of neon; that of Soddy and Hyman[62] on lead from thorium and ordinary lead, and finally those of Richards and Lembert,[63] Hönigschmidt and St. Horivitz,[64] and of Merton,[65] on radium G and ordinary lead. Merton used a grating, and finally a Fabry and Perot étalon, and concluded from his work with the latter that there is no difference in wave-length as great as 0.003 A. for the line λ4058 in the spectrum of ordinary lead and of radium-G.

However, it should be noted that most of these investigators were precluded from the discovery of the shift in question by the lack of sensitiveness of the spectrographs at their command, whereas in the work in Chicago the Michelson 10-inch grating with a 30-foot Littrow mounting was used in the sixth order.

The shift found experimentally is 100 times greater than that predicted by Bohr's equation[66]

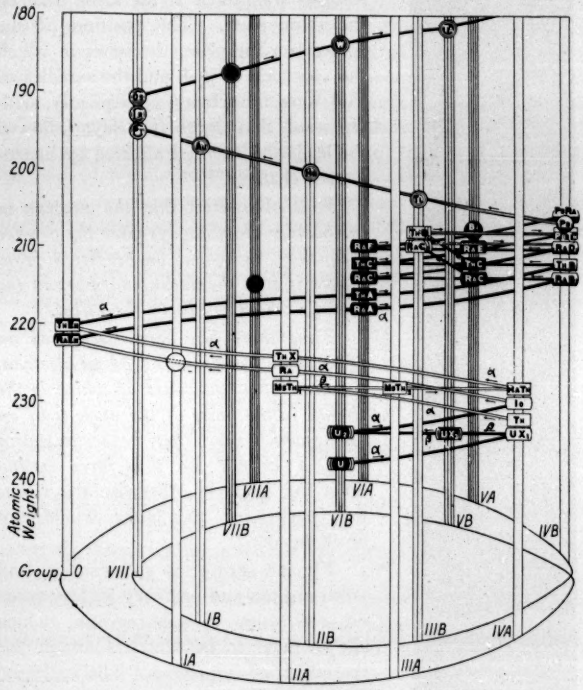
$$\nu = \frac{2\pi^2 e^2 E^2 mM}{h^3 (M+m)} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

and enormously greater than that indicated by the simple gravitational theory. The discovery of the effect was brought about by the idea of the writer that there should be a slight difference in the spectra of isotopes other than the extremely simple mechanical effect suggested by Fowler[67] and given in Bohr's equation. First, differences in the placing of the positive and negative electrons inside the nucleus should make the attractive force between an electron and the nucleus different in different isotopes, although it seemed not unlikely that this might produce such a small effect in the spectral lines as to make its detection impossible. Second, it seemed not improbable that

[59] *Proc. Roy. Soc.* (*London*), **87**, 478 (1912).
[60] *Sitz. Akad. Wiss., Wien* (*Abt. IIa*), **121**, 175 (1912).
[61] *Brit. Assoc. Meeting*, **1913**, p. 403.
[62] *J. Chem. Soc.*, **105**, 1402 (1914).
[63] *J. Am. Chem. Soc.*, **36**, 1329 (1914).
[64] *Sitz. Akad. Wiss., Wien* (*Abt. IIa*), **123**, Dec. (1914).
[65] *Proc. Roy. Soc.* (*London*), **91**, 198 (1914).
[66] Bohr: *Nature*, **92**, 231 (1913).
[67] Fowler: *Nature*, **92**, 95 (1913).

at such a minute distance as that between a nucleus and a planetary electron, the mass of the nucleus might attract the electron much more greatly than corresponds to the simple inverse square law; particularly if gravitation has an electromagnetic origin.

FIG. 27.



Periodic system of the elements radioactive portion.

The source of light used was a lead arc in a vacuum of 0.04 mm. pressure of lead vapor. Such an arc was used first, but with other metals, by Wali-Mohammed. The current was 1.1 amperes and the voltage 40, but a variation in the voltage and current was found to produce no change in the position of the

lines. Fig. 24 is a diagram of the apparatus used. The anode of lead was held in place by a porcelain tube. Two such arcs, one containing ordinary and the other isotopic lead, were run side by side at the same pressure, and the spectrum of both samples was taken at the same time on the same plate. The position of the spectra on the plate, the tubes in which the arcs were placed, and the samples of lead were interchanged frequently, with the result that the shift always followed the lead, and was not affected by instrumental changes.[68]

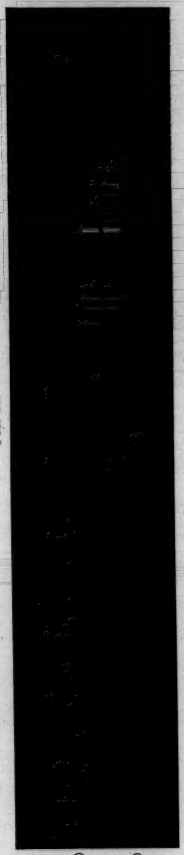


FIG. 28.—Spectrum of lead (*a*) and radio-lead (*b*).

It is of interest that *the electron in the heavier atom always gave the greater frequency, as would be predicted from theory if it is the additional mass in the nucleus which produces the effect.*

Thus there has been discovered an effect upon the vibration of an electron, the most apparent cause of which is the change in the mass of the nucleus of an atom, which must then be accompanied with a change in the force acting upon the electron, otherwise the vibration period of the latter would not be changed.

Fig. 28 shows the spectrum of lead from radium and ordinary lead as taken on an ordinary spectrograph, which shows them to be identical except for the effects of impurities. The lead used in the experiments with the grating was very much more highly purified than that from which the photograph was obtained. The dispersion used with the grating was so high that few lines were found on the plate.

[68] Merton [*Proc. Roy. Soc. London*, **96A**, 388–95 (1920)] has confirmed the experimental results both with respect to magnitude and sign.

52. NON-IDENTITY OF ISOTOPES IN CHEMICAL PROPERTIES.

The slight differences found in the vibration frequencies of the light given off by isotopes indicates that the electrons are not held by identical forces, *so isotopes should not be identical from the chemical standpoint,* though the minute difference found in wave-length (0.0001 per cent.) shows clearly that the chemical means now available are not capable of detecting the difference in the properties of the isotopes of lead. It is quite possible, when the difference in mass of the isotopes is as high as 16 per cent., as is the case with Li^6 and Li^7, that the chemical differences would be sufficient to be apparent to the most delicate tests. This evidently depends upon how the magnitude of the effect varies with the mass of the nucleus, which is at present entirely unknown.

Richard's [69] has shown in very precise experiments that the atomic volumes and melting points of ordinary lead and lead from radium are the same within the limits of the experimental errors. *The wave-length of the spectrum lines is the first chemical property with regard to which isotopes have been found to differ.*

53. SPECTRA AS A MEANS OF DISTINGUISHING BETWEEN ISOTOPES.

It is evident, if isotopes give slightly different spectra, that they may be distinguished by the use of delicate spectroscopic apparatus. It might seem also that the presence of isotopes in a mixture might be thus detected, but the latter supposition was not found justified in the case of lead, though it may be by later work on lighter isotopes. Both specimens of lead gave a line of about the same width, and this line was shifted as a whole, a remarkable result if ordinary lead is, as it is usually supposed to be, a mixture of isotopes of atomic weights 206 and 208. Also, even if ordinary lead should be an individual isotope, the radium lead used contained about 30 per cent. of ordinary lead, so on the basis of either hypothesis a mixture was used.

(To be concluded.)

[69] T. W. Richard's "Presidential Address to the American Association for the Advancement of Science" (1918), *J. Am. Chem. Soc.*, **38**, 221 (1916).

The Yield of Glucose from Cotton Cellulose.—IRVINE and HIRST (*J. C. S.*, 1922, vols. 121–2, 1885) made an investigation with a view of determining the reason that the usual processes for converting cellulose into glucose do not give the yield that would be expected upon the theory that cellulose is composed entirely of glucose units. Previous investigations by Irving and Soutar in 1920 had given a yield of 85 per cent. The experiments now reported were carried on upon the same general principles as the former ones, but a notable improvement was obtained by conducting the acetolysis in the manner suggested by Barnett (*J. S. C. I.*, 1921, v. 40). An excellent yield of cellulose triacetate of uniform quality was obtained, and as no sugar was found in the washings, much work was eliminated. The conversion of the acetate into methylglucoside was performed in many ways, but for quantitative work of this kind, the best results were obtained by digesting small amounts of the compound with methyl alcohol containing about 0.75 per cent. hydrogen chloride. The use of an autoclave was abandoned, the whole procedure being carried out in sealed tubes, containing about 4 grams of the triacetate. After about seventy hours' action only a trace of solid matter remained, and the solution, which was faintly yellow, contained alpha- and beta-methylglucosides in equilibrium. The specific rotation of the liquid ranged within 107–108°, the calculation being based on the assumption that the whole of the cellulose has been converted into the methylglucoside.

Each of the reactions involved has been carried out on numerous occasions and by independent workers. With practice and experience the yields have been regular, and the following figures are submitted as the average of the concordant experiments:

Cotton cellulose	100	parts
Cellulose triacetate	117	parts
Methylglucosides	114.1	parts
Equivalent of glucose	106	parts

The yields are in each case about 99.5 per cent of the theoretical.

H. L.

Minimum Sound Energy for Audition for Tones of High Frequency. C. E. LANE. (*Phys. Rev.*, May, 1922).—For frequencies ranging from 2000 to 14,000 per second it was found that, in order to produce the sensation of sound there must flow through a square centimetre in a second an amount of sound energy equal to 7×10^{-8} ergs. This quantity is practically the same for the range of frequencies specified, though small differences exist not only between individuals but even between the two ears of the same person. Above 14,000 per second more and ever more energy is needed for the production of the sensation until, at some frequency between 18,000 and 20,000, according to individual idiosyncrasy, 1,400,000 times as much energy as was adequate at the lower pitch does not produce any sensation. This upper frequency limit is highest for children and lowest for old people.

G. F. S.

NOTES FROM THE LABORATORY OF PURE SCIENCE, NELA RESEARCH LABORATORIES.*

SHORT ELECTRIC WAVES.

By E. F. Nichols and J. D. Tear.

[ABSTRACT.]

THE present experiments were undertaken in the hope that by devising improved instruments and better and more accurate methods for experimenting with short electric waves, further progress might be made in narrowing the still unexplored region of the spectrum which extended from a wave-length of 0.3 mm. to one of about 10 mm., and in making the results of future short electric wave experiments more nearly quantitative and trustworthy.

The source of radiation finally adopted is a modified form of Hertzian doublet, embodying a number of new features making possible the generation of very short waves. A disruptive discharge is caused to pass between two tungsten cylinders immersed in kerosene. The cylinders, of which the smallest used were 0.2 mm. long and 0.2 mm. in diameter, were held in place by being sealed into the closed ends of hard glass tubes which were mounted with micrometer adjustments, enabling the spark gap between the two halves of the doublet to be accurately controlled. High potential leads enter through the glass tubes and are brought within a few millimetres of the outer ends of the tungsten cylinders, leaving short air gaps for the discharge to cross. Streams of compressed air keep these air gaps deionized and free from oil and also serve to cool the glass-tungsten seal. When the gap in oil between the two cylinders is of the proper length (about .01 mm.) each discharge sets up electrical oscillations in the doublet, causing it to emit a highly damped radiation, the fundamental wave-length of which is determined by the dimensions of the doublet and by the dielectric constants of the surrounding media, *i.e.*, oil and glass. In practice the fundamental wave-length emitted by the doublet was found to

* Communicated by the Director.

be from three to five times the overall length of the doublet, the larger factor applying to the smaller doublets.

The source is mounted on an optical bench at the principal focus of a paraffin lens. The radiation emerging from this collimating lens in a beam of parallel rays passes through the interference apparatus or whatever optical system is in use at the time, and is then collected by a second lens and brought to a focus upon the vanes of the receiving instrument.

By adapting the Nichols radiometer to electric wave reception an enormous increase in sensitivity over earlier electric wave receivers has been obtained. This increased sensitivity is due in part to the particular receiving elements chosen for the resistance-absorption of the incident radiation; in part to the substitution of the radiometer method for the less direct thermocouple galvanometer method of measuring small amounts of energy; and again in part to further improvements in radiometer technic. A number of minor changes in the form of radiometer suspensions have been made, and a considerable decrease in weight has been achieved, making possible the use of much finer quartz fibres. The total weight of some of the smaller suspended systems was about 0.5 mg.

Receiving elements, either of 1μ platinum wire of proper length for resonance with the incident radiation, or of metallic films deposited upon thin mica strips or quartz fibres by the evaporation method, are substituted for the usual blackened radiometer vanes. Thin mica shields are so mounted about 0.1 mm. in front of or behind the receiving elements as to make the radiometer action of the two vanes unilateral.

Wave-length measurements were made with the Boltzmann mirror interferometer and also with a reflecting echelon or flight of steps, made of carefully machined brass blocks so mounted as to be easy of adjustment to any desired spacing, width, or thread. The echelon was also used for obtaining an approximate analysis of the radiation emitted by the Hertzian doublet and to separate out more homogeneous radiation of a desired wave-length.

By the foregoing procedure electric waves from several centimetres down to 1.8 mm. in length have been isolated. Under

favorable conditions a wave-length of 0.8 mm. has been observed. The known electric wave spectrum has thus been extended toward shorter waves by an interval of from two to three octaves.

THE OPTICAL CONSTANTS OF CERTAIN LIQUIDS FOR SHORT ELECTRIC WAVES.

By J. D. Tear.

[ABSTRACT.]

IN crossing the hitherto unexplored region of the spectrum extending from the extreme infra-red to the shortest electric waves, the reflection and absorption coefficients and the indices of refraction of a number of liquids undergo unusual changes. A notable example is water which for λ0.3 mm. has an index near that for the visible region of the spectrum, but for λ30 mm. has a refractive index of 8.5, which is very nearly that for an infinite wave-length, *i.e.*, the square root of the dielectric constant. Experiments, described in the preceding abstract,[1] are now in progress which, it is hoped, will ultimately make a more complete exploration of this region possible. With the present equipment and methods the optical constants of a number of liquids, *i.e.*, water, glycerin, methyl and ethyl alcohol for the wave-lengths 4, 8, 11, 18, and 27 mm., have been determined.

The refractive indices have been computed by the Cauchy-Quincke formula from measured values of the coefficients of reflection and absorption. A second approximate, though direct determination of the refractive index, has been obtained by measuring the combined reflection from both surfaces of a thin liquid layer floated on mercury. As the thickness of the layer is varied, interference effects cause the reflected energy to pass through a series of maxima and minima which give a direct measurement of the wave-length in the liquid which divided into the wave-length in air gives the refractive index. The results obtained by these two methods are in good agreement.

The Thermal Stresses in Solid and in Hollow Circular Cylinders Concentrically Heated. CHARLES H. LEES. (*Proc. Royal Soc.*, A 712).—"The large differences of temperature which exist between the inside and outside of the heating or firing tunnels used in pottery and

[1] E. F. Nichols and J. D. Tear, "Short Elecrtic Waves."

other works, and between the inner and outer portions of the concrete or masonry pillars supporting the floors of a building in which a fire occurs, make the thermal stresses approach the breaking strength of the materials and they are crushed or torn asunder." These stresses have hitherto been calculated only under the assumption of certain limiting simplifications. The author solves the problem in a more general way and shows "that for any temperature distribution, with any law of expansion, the stresses may be found by a simple graphical method so long as the variation of the elastic constants with the temperature may be neglected."

After the problem has been solved the solution is applied to definite cases occurring in industry such as the putting out of service of a pottery kiln. "The sudden cooling of the interior of a furnace such as that described above will therefore subject the interior of the wall to tensile stresses in both longitudinal and tangential directions much above the tensile strength of the material, and radial cracks will be produced at the inner surface, which, since the stresses are equal in the two directions, will run indiscriminately longitudinally and tangentially. Through the kindness of Sir Robert Hadfield I have been able to inspect the walls of furnaces which have been in use for various periods at the Hecla Works, Sheffield, and I find that the above results are confirmed by experience." An explanation is furnished also of the cracks which exist within columns that have been subjected to fire and which do not show themselves at the surface.

This paper will in the future be used in the design of structures.

G. F. S.

The Dielectric Constant of Mica. J. R. WEEKS, JR. (*Phys. Rev.*, April, 1922).—Eighteen samples of mica of twelve different grades were measured. For sheets without visible air films the value of the constant was found to range from 6.4 to 9.3. Sheets having included air films seemed to give values from 2.9 to 5.6. Thin sheets split from the sample which had given 2.9 were measured and the results varied from 6.6 to 8.4. Other similar experiments confirm the belief that the low results are to be attributed to the presence of air. Thus is probably explained the wide divergence between values of the dielectric constant of mica given in handbooks.

G. F. S.

The Departure from Ohm's Law in Gold and Silver at High Current Densities. P. W. BRIDGMAN. (*Phys. Rev.*, April, 1922).—A method has been devised of attaining current densities of 5,000,000 amperes per sq. cm. along with the possibility of correcting the resistance for the increase of temperature. With these high current densities the resistance was found to increase about 1 per cent., the proportional increase being larger in thick than in thin gold and also greater for gold than for silver.

G. F. S.

NOTES FROM THE RESEARCH LABORATORY, EASTMAN KODAK COMPANY.*

THE 6-ALKYLOXYQUINALDINES.[1]

By H. LeB. Gray and G. O. Gutekunst.

[ABSTRACT.]

THE preparation of the 6-alkyloxyquinaldines involved the preparation of relatively large quantities of the paraminophenyl alkyl ether either by (1) preparation of the paranitrophenyl alkyl ether and reduction to the amino compound or (2) preparation of the paraceto-aminophenyl alkyl ether and hydrolysis by means of sulfuric acid. Several of the paranitrophenyl alkyl ethers had been previously prepared by heating for six hours the potassium salt of paranitrophenol in 16 per cent. alcoholic solution with the desired alkyl bromide or iodide in an autoclave at 170°–180° C. These ethers were prepared by boiling under a reflux for twelve hours a solution of the potassium salt of paranitrophenol in aqueous alcohol and the desired alkyl bromide or iodide. In a few cases the addition of the corresponding alcohol was necessary. The aceto-aminophenyl alkyl ethers were prepared in the same way, starting with paraceto-aminophenol. The following undescribed compounds were prepared: Paranitrophenyl butyl ether, fine white needles from alcohol, M. P. 32°; paraminophenyl butyl ether, light yellow oil boiling at 143°–144° at 12 mm.; paranitrophenyl iso-amyl ether, pale yellow oil boiling at 183° at 18 mm.; paraminophenyl iso-amyl ether, pale yellow oil boiling at 149°–150° at 15 mm.; paraceto-aminophenyl allyl ether, minute crystals from benzol, M. P. 88°–89°; paraminophenyl allyl ether, light yellow oil boiling at 143°–144° at 13 mm.; paraceto-amino phenyl butyl ether, white needles from benzol, M. P. 112°; paraceto-aminophenol benzyl ether, white needles, M. P. 142°; paraceto-aminophenyl iso-butyl ether, white needles, M. P. 80°–81°; paraminophenyl iso-butyl ether, colorless oil boiling at 145°–146°, at 10 mm.; paraceto-aminophenyl iso-amyl ether, white plates

* Communicated by the Director.

[1] Communication No. 138 from the Research Laboratory of the Eastman Kodak Company and published in *J. Amer. Chem. Soc.*, August, 1922, p. 1741.

from benzol, M. P. 102°–103.5°; (the quinaldines were prepared by the Doebner-Miller quinaldine synthesis) 6-propyloxyquinaldine, light yellow liquid boiling at 176°–177° at 16 mm.; 6-propyloxyquinaldine ethiodide, pale yellow needles from ether alcohol, M. P. 147.5°; 6-allyl oxyquinaldines, red oily liquid; 6-allyl oxyquinaldine ethiodide, small yellow needles from ether alcohol; 6-butyl oxyquinaldine, yellow needles from petroleum ether, soften at 48° and melt at 52°; 6-butyl oxyquinaldine ethiodide, yellow needles from ether alcohol, M. P. 186°; 6-iso-butyl oxyquinaldine, colorless oily liquid boiling at 171°–172° at 12 mm.; 6-iso-butyl oxyquinaldine ethiodide, yellow needles from ether alcohol, M. P. 142°; 6-iso-amyl oxyquinaldine, light yellow liquid boiling at 182°–183°, at 10 mm.; 6-iso-amyl oxyquinaldine ethiodide, yellow needles from ether alcohol, M. P. 201°.

PRELIMINARY INVESTIGATIONS ON SILBERSTEIN'S QUANTUM THEORY OF PHOTOGRAPHIC EXPOSURE.

By A. P. H. Trivelli and L. Righter.

[ABSTRACT.]

THIS is a paper on the experimental investigation of the light quantum theory recently proposed by Doctor Silberstein.[3] The experiments were intended primarily for a study of the effect of clumping of silver halide grains in a photographic emulsion. It was found that clumps acted as single grains for development to the limit, thereby giving a very large range of grain sizes. These data afford a very rigorous test for Silberstein's theory which is essentially:

$$\frac{k}{N} = 1 - e^{-na}$$

where N is the original number per unit of the plate, of the class of size (area) a, n the number of incident light quanta, again per unit area of plate, and k the number of grains effected.

A brief description of the experimental procedure and table of results are given. The agreement of the observed results with those calculated from Silberstein's formula is very pronounced.

[3] Communication No. 141 from the Research Laboratory of the Eastman Kodak Company and published in *Phil. Mag.*, July, 1922, p. 252.

[3] *Phil. Mag.*, 1922, p. 257.

NOTES FROM THE U. S. BUREAU OF CHEMISTRY.*

A METHOD FOR THE DETERMINATION OF AMINO NITROGEN AND AMMONIA IN CREAM AND BUTTER.[1]

By L. W. Ferris.

[ABSTRACT.]

In order to measure the relative proportion of amino nitrogen in milk, cream, buttermilk, and butter, it is desirable to have a procedure that is adaptable to all of these products. A method using picric and acetic acids, devised in the Bureau of Chemistry, has the following advantages:

1. Easy and rapid separation of the proteins and more complex substances from the lower degradation products, principally amino acids.

2. Hydrolysis of proteins during analysis is reduced to a minimum.

3. The filtrate can be held without further change, allowing a reasonable time between preparation of sample and analysis.

4. A correlation between amount of amino nitrogen and quality of sample.

By this procedure the amino nitrogen and ammonia in fourteen samples of fresh butter from sweet cream was found to range from 0.9 to 2.3, with an average of 1.4, expressed as percentage of the total nitrogen.

STUDIES ON THE DIGESTIBILITY OF PROTEINS IN VITRO. III. ON THE CHEMICAL NATURE OF THE NUTRITIONAL DEFICIENCIES OF ARACHIN.[2]

By D. Breese Jones and Henry C. Waterman.

[ABSTRACT.]

ESTIMATIONS of the digestibility *in vitro* of variously treated preparations of arachin (the principal protein of the peanut, *Arachis hypogæa*) by the method of Waterman and Johns, indicate: (1) That this protein is incompletely digestible, and that

* Communicated by the Chief of the Bureau.

[1] Published in *J. Dairy Sciences*, 5, July, 1922, 399.

[2] Published in *J. Biol. Chem.*, 50, June, 1922, 357.

this condition is not altered by boiling with water at ordinary pressure or by cooking under a steam pressure of fifteen pounds; and (2) that the nutritional failure of arachin is due to the retention of a considerable part of one or more of the essential animo acids, the most conspicuous of which is histidine, in the indigestible complex. The total amino acid composition of arachin would almost certainly be quite adequate, if it were available.

A direct comparison of the digestibility *in vitro* of arachin with that of casein and of cooked phaseolin gave the following (average) values for percentage of digested nitrogen, calculated on the basis of the total amino, *minus* free amino nitrogen: Arachin, 48.5; casein, 61.4; cooked phaseolin, 58.7. The control proteins are known to be sufficiently digestible to be available. An extremely indigestible partial cleavage product, produced by warming arachin with 0.1 N sodium hydroxid for two hours and precipitating the unattacked residue with very dilute acid, contained somewhat more than two-thirds of the total histidine, and about two-fifths of the total lysine of the arachin from which it was derived.

The experiments indicate that the incomplete digestibility of arachin is not due to changes brought about by the treatment involved in its isolation, but is a native property of the protein. The high nutritional efficiency of peanut meal is therefore to be attributed to the presence in the meal of sources of amino acids which supply essentials contained in an unavailable form in arachin.

THE PLAGIOCLASE FELDSPARS AS A CASE OF ATOMIC ISOMORPHISM.[1]

By Edgar T. Wherry.

[ABSTRACT.]

THE structural formula viewpoint is incapable of accounting for the isomorphism of the plagioclases, the arithmetical viewpoint mistakes a corollary for a cause, and only the atomic isomorphism viewpoint really corresponds to the data. As sodium is indicated by X-ray measurement to occupy approximately the same volume as calcium, and aluminium as silicon, the two feld-

[1] Published in *Am. Mineralogist*, 7, July, 1922, 113.

spars may well have identical geometrical structures; the valence relations in solution merely require the one replacement to be accompanied by the other, and do not persist into the solid form of the compounds. Orthoclase and carnegieite can not be isomorphous with anorthite because the potassium atom of the one, and still more the two sodium atoms of the other, demand more space than displacement of the calcium can furnish. The simplest formulas adapted to bring out all the relations are: Albite, $NaAl(Si_3O_8)$; anorthite $CaAl(AlSi_2O_8)$.

Additions to Research Staff of the Eastman Kodak Company.—The following experts have recently been added to the laboratory of this company: Dr. Helge Schibsted, formerly with the Atmospheric Nitrogen Company; Clyde Brockett and D. H. Harris, Massachusetts Institute of Technology, 1922; A. Burgess, Bates College, 1922; R. P. Loveland, Grinnell College, 1922. H. L.

The Frequency-Sensitivity of Normal Ears. H. FLETCHER and R. L. WEGEL. (*Phys. Rev.*, June, 1922).—The sensitivity of the ear is here given in terms of the alternating (root mean square) pressure requisite for the production of a minimum audible sensation. "A tone of 1000 cycles per second requires only one-sixtieth as much pressure variation for audition as a tone at 100 cycles per second. The average sensitivity for normal ears varies from .15 dyne at 60 cycles to .001 dyne at 1000 cycles. Between 1000 and 4000 cycles the sensitivity is approximately constant and equal to .001 dyne per square cm."

An inspection of the curves connecting pitch and sensitivity in terms of pressure leads to the thought that individual differences are as sharply characteristic as they are in thumb prints. For instance, one person manifested a remarkable drop in sensitivity at 3000 cycles, and this held for both ears, though until 4500 cycles was reached the left ear exceeded its fellow in sensitivity. For the range of frequencies used in speech the following relations are stated: "Persons who have normal hearing require approximately .001 dyne per square centimetre in order to hear sounds in this range. Persons who require pressure variation of .1 dyne per square centimetre are called slightly deaf. Those who require one dyne are partially deaf but can usually follow ordinary conversation. Those who require 10 dynes belong to that class who use ear trumpets or deaf sets to amplify the speech waves. A pressure variation of approximately 1000 dynes can be felt and produces a sensation of pain.

"This shows that among people who can follow ordinary conversation there is a range in ear sensitivity of more than 1000 and among people who are noticeably deaf there is another range of 1000, making a total range of more than a million for people who can hear or be made to hear by means of amplifying devices." G. F. S.

Manufacture of Carbon Disulphide in the Electric Furnace.—George A. Richter of the Research Department of Brown and Company, Berlin, N. H., contributed to the forty-second general meeting of the American Electrochemical Society a paper embodying the results of experiments on the production of carbon disulphide by the Taylor process, although differing somewhat from the original form of that process. Large-scale production of the substances is based upon the direct action of the two elements at a temperature ranging from 600 to 1000° C., at which temperature the sulphur is, of course, in the form of vapor and the carbon an incandescent solid. Not all forms of carbon are admissible; anthracite, gas coke and other dense forms cannot be used. Good grades of willow or birch charcoal are among the best, especially those with a low ash content. The materials should be as dry as practicable. Water vapor will form hydrogen sulphide and other sulphur compounds. The charcoal should be well burned. The mechanical arrangements are described in the article, and the thermal data are presented in much detail. The conclusions are that a comparatively recent process for the manufacture of carbon disulphide has been devised and actual plant data indicate that the unit operates with reasonably fair thermal efficiency.

H. L.

Magnetostriction with Small Magnetizing Fields. J. R. HOBBIE, JR. (*Phys. Rev.*, May, 1922).—Joule as long ago as 1847 studied the change in length of a piece of iron upon the application of magnetic forces. Later Bidwell found that iron grew longer until a certain magnetizing force was attained. After this point it shortened. Nickel, on the other hand, contracted from the first application of force and no magnetizing field caused it to do anything but contract.

This investigation is limited to a study of magnetostriction with small fields. No new results came to light that are of a striking character. The importance of the work lies in this. Previous investigators in this field have been able to detect a change of length of one part in one hundred million while here three parts in a billion billion can be noticed. The sensitiveness has been made three thousand fold as great.

The piezo-electric properties of quartz and of Rochelle salt were made use of. The wire under examination hung from the crystal and was magnetized by a coil carrying an alternating current. The alternating magnetic field set up periodic changes in the length of the wire and the crystal was subjected to corresponding changes of tension, which, in turn, produced an alternating electromotive force between its tinfoil coatings. From a study of this it was possible to infer the extent of the changes of length of the wire. The method has the weakness that it does not discriminate between an elongation and a contraction due to the field.

A careful search was made for electrostriction in bismuth, but no trace of it was found. G. F. S.

NOTES FROM THE U. S. BUREAU OF MINES.*

EXPERIMENTAL PRODUCTION OF ALLOY STEELS.

By H. W. Gillett and E. L. Mack.

THE Bureau of Mines has prepared a number of series of alloy steels for the Army and Navy, the Vanadium Corporation, and the Welsbach Company, containing such alloying elements as uranium, vanadium, tungsten, molybdenum, cerium, boron, and zirconium, alone and in various complex alloys. The steels prepared were studied with reference to the alloy recovery, the character and composition of the ingot, and their metallurgical behavior in the furnace. The Bureau of Standards and a number of commercial steel companies have coöperated in this work.

Some of the conclusions derived from this work are as follows:

The use of a small direct arc furnace for making small experimental heats of alloy steel is attended with difficulty because of the carbon content. Indirect arc types allow much better control of the carbon.

Since the composition of many of the steels prepared is suitable only for special use, no direct conclusions can be drawn as to the value or lack of value of zirconium, titanium, uranium, boron, and cerium as true alloying elements in commonly used types of steels. The results of the physical tests so far have not in general been promising.

Even in very small ingots of 50 to 100 pounds, notable segregation of uranium, zirconium, or cerium generally appears when over about one-half per cent. of the first, or about one-third per cent. of either of the two latter is present in the steel.

These readily oxidizable elements are best added in the ladle, or to the furnace immediately before pouring. In remelting scrap containing these elements, they will be almost wholly lost, even in electric-furnace melting.

Uranium, and especially zirconium alloys used to introduce these elements into steel, should apparently be as free from carbon as possible. Alloys of zirconium with silicon or nickel, or both,

* Communicated by the Director.

give fair recoveries of zirconium, but no ferrozirconium tried does.

Titanium does not segregate as readily as zirconium, and its recovery from the ferro is higher; but in large amounts it is likely to segregate, and its recovery is not usually quantitative, although it may be quantitative if it is protected by the presence of a more readily oxidizable element, such as zirconium.

Although these elements are readily oxidized, none of them appears to be as efficient as aluminum or vanadium in degasifying "wild" steel. No special study has been made of very small amounts of these elements used as scavengers only, but all seem likely to leave their oxides or other compounds trapped in the steel as inclusions when added immediately before pouring, as is necessary in order to get a good recovery when using them as alloying elements rather than as scavengers.

Boron is almost quantitatively recovered when added at the end of the heat, and may be added at the start of the heat without great loss. In the amounts studied up to 0.6 per cent., no appreciable tendency to segregation was noted.

Further information on the tests will be found in Bulletin 199, recently issued by the Bureau of Mines.

INCLUSIONS IN ALUMINUM ALLOY SAND CASTINGS.

By Robert J. Anderson.

ON account of the difficulty experienced by many aluminum-alloy foundrymen in eliminating hard spots from aluminum alloys, with resulting trouble in machining the casting, the Bureau of Mines made a study of inclusions in castings, with a view to putting the available knowledge of different operators on record and suggesting preventive methods.

The results indicate that the losses from hard spots are sufficiently serious to require the careful attention of all foundries, but the experience of many of the foundries has shown that close attention to certain aspects of foundry practice may substantially prevent their occurrence, particularly in preventing foreign materials, such as dirt, pieces of crucibles, etc., from being charged with the floor cleanings and scrap.

The results are more fully described in Technical Paper 290 of the Bureau of Mines.

CORROSION UNDER OIL FILMS, WITH SPECIAL REFERENCE TO THE CAUSE AND PREVENTION OF THE AFTER-CORROSION OF FIREARMS.

By Wilbert J. Huff.

Toward the end of the World War, the Bureau of Mines was requested to investigate the causes of after-corrosion upon the bore surfaces of the infantry service rifles, with the ultimate purpose of developing some simple procedure for eliminating this serious menace. The Bureau was especially fitted for conducting such an investigation because of its previous work on the preservation and utilization of our metal resources, and because of the experience of certain of its members in explosives and oils. Experiments had hardly begun when the Armistice was signed, but as the problem is important because of its applications both in war and in peace, continuance of work on it was deemed advisable. The Ordnance Department of the Army says that probably more rifles are ruined by improper preparation for storage than by any other cause; and the problem, though primarily military, touches the interest of every owner of a firearm.

The importance of this study is not, however, limited to the users of firearms. The fundamental problem proved to be corrosion under oil films; this differentiates after-corrosion sharply from the ordinary corrosion of clean iron and steel surfaces. It was found that this after-corrosion is closely allied to a number of other general problems, such as the corrosion under oil of bright steel parts after handling in manufacturing operations, and to the corrosion under oil experienced near the ocean.

A critical laboratory study, comprising the exposure of fired rifles and fouled barrel sections to known humidities, the chemical examination of the corrosive residue, the use of special ammunition, and the analysis and testing of many "nitrosolvents" and other compositions recommended as preventives showed:

The present high-pressure smokeless cartridge leaves no nitrocellulose residue and no corrosive acid residue. After-corrosion following the use of such cartridges is caused by (1) the explosive deposition of a water-soluble salt or salts in whose aqueous solution the steel corrodes, together with subsequent exposure to (2) a high humidity and (3) the presence of oxygen. In the present service ammunition this salt is potassium chloride from the decomposition of the chlorate in the primer.

Such water-soluble salt or salts are retained in tool wounds and pits on the bore surfaces, in which they can not be seen and from which they can not be removed mechanically. They are easily dissolved by water or suitable aqueous solutions.

After-corrosion may also be prevented by keeping both ends of the bore tightly corked.

The present service ammunition can be rendered non-corrosive by eliminating the chlorate of the primer. It may be possible to develop a non-corrosive primer that will not affect the present ballistic properties of the cartridge. This point is under investigation.

A number of non-aqueous compositions recommended for cleaning firearms possess little or no value. Their supposed virtue seems to rest on tests conducted at humidities so low that no corrosion could occur.

After-corrosion proceeds below the dew point.

A simple test for differentiating between worthless and valuable cleaning compounds was devised.

Further information may be found in the report on the results of this work, published as Technical Paper 188 of the Bureau.

Prototypes of the International Ohm. Paul Janet. (*Comptes Rendus*, July 10, 1922.)—In the years following the conference held in Washington in 1910 for the consideration of the silver voltameter and for the fixing of the ampere, many of the national physical laboratories have constructed standard mercury ohms. Even before this René Benoit, who made the standard ohms for France in 1883, had announced his intention of resuming this type of work and of preparing 10 mercury standards. This he set about, not as his duty as the official head of the International Bureau of Weights and Measures, but as a scientific labor of love. After his tubes had been selected and calibrated they were transported to the Central Electrical Laboratory where a special apparatus for the distillation of mercury in vacuum had been installed. The process of filling them with the liquid in a vacuum had been completed and the ohm standards were ready for measurement when the war broke out. During the bombardment of Paris by the invaders these precious products were carefully protected. It was not till 1919 that work was resumed. Then it was deemed necessary to refill them. The eight tubes that have stood all tests have now been completely determined. On the average the divergence between the resistance calculated from their dimensions and the measured resistance amounts only to nineteen millionths. How much care, labor and scientific acumen have been needed to bring to a successful termination this long series of processes is known only to the metrologist. G. F. S.

THE FRANKLIN INSTITUTE.

(*Proceedings of the Stated Meeting held Wednesday, October 18, 1922.*)

HALL OF THE FRANKLIN INSTITUTE,

PHILADELPHIA, October 18, 1922.

MR. W. C. L. EGLIN, Vice-president of the Institute, *in the Chair*.

The Board of Managers submitted their report. The report recorded the elections to membership of:

Murray C. Boyer, Esq., Solicitor of Patents, 806 Franklin Trust Building, Philadelphia, Pennsylvania;

Roland L. Eaton, Esq., 20 South Eighteenth Street, Philadelphia, Pennsylvania;

Joseph F. Greene, Esq., B.S., Chemical Engineer, Kimble Glass Company, Vineland, New Jersey;

Robert Hatfield Irons, Esq., President, Central Iron and Steel Company, Harrisburg, Pennsylvania;

Ernest Edward Johnson, Esq., B.S., M.S., Professor of Physics, Northeast High School, Philadelphia, Pennsylvania;

William B. Leighninger, Esq., B.A., M.A., Teacher of Chemistry, Frankford High School, Philadelphia, Pennsylvania;

John E. Symons, Esq., Mechanical Engineer, The Texas Company, New York City, New York;

James A. Wright, Wright-Fisher Engineering Company, Detroit, Michigan;

a lecture before Sections by

Herbert E. Ives, Ph.D.,
Research Laboratories,
The American Telephone and Telegraph Company and Western Electric Company, Incorporated, New York City, New York,

on "The Primary Standard of Light";

and additions to the library by gift, 322 volumes and 356 pamphlets; by purchase, 68 volumes and 1 pamphlet and by binding, 272 volumes.

The Board of Managers also transmitted the following preambles and resolution prepared by a special committee appointed by them to consider, at the request of the Board of Trustees, the advisability of certain changes in the By-Laws:

WHEREAS, doubt has arisen as to the meaning of the following provisions of Section 1 and Section 6 of Article 1 of the By-Laws, namely, the words "In the way and manner hereinafter provided so that the same shall not in any event be liable for the debts of the Institute," after the word "Institute" (Section 1), and the last paragraph of Section 6 as follows: "The principal and interest of all trust funds shall not be liable for debts of the Institute but shall be devoted to

its continuance and preservation," and counsel having advised that in their opinion the principal and income from the unlimited trust estates may be applied by the Board of Trustees to the current expenses and obligations, or other legal purposes of the Institute, but advise that the By-Laws should be amended so that all doubt with respect to such power should be removed,

AND WHEREAS, so that the purposes of the use of these trust funds as affected by the By-Laws may be clear of doubt;

Resolved, that the words "in the way and manner hereinafter provided so that the same shall not in any event be liable for the debts of the Institute," in Section 1 of Article 1 be omitted and stricken therefrom, and that the last paragraph of Section 6 of Article 1, as follows: "The principal and interest of all trust funds shall not be liable for debts of the Institute but shall be devoted to its continuance and preservation," be omitted and stricken therefrom, and that Section 1 of Article 1 and Section 6 of Article 1 be amended so as to read as now expressed with the omission of the said words,

and recommended to the Institute their adoption.

Doctor Hoadley moved that the recommendations of the Board of Managers as to amendments to Sections 1 and 6 of the By-Laws of the Institute be voted on at the next Stated Meeting in accordance with Article 17, By-Laws of the Institute. This was duly seconded and unanimously carried.

The Board further reported that at their meeting held on the afternoon of Wednesday, September 13, 1922, Mr. W. C. L. Eglin was elected Vice-president of the Institute to serve until the next regular election of officers in January. It was explained that the need for this action was occasioned by the absence of Dr. Walton Clark, President, and the death of Mr. Coleman Sellers, Jr., Vice-president; also it was pointed out that while the By-Laws embody no specific provision for the election of a Vice-president before the annual meeting of the Institute, the Institute's attorneys, Messrs. Brown and Williams, advised that presumably the power to fill a vacancy is vested in the Board of Managers, subject to ratification by the Institute. The matter of confirming this election was then presented to the Institute for action.

On motion of Doctor Alleman, seconded by Doctor Keller, the election of Mr. W. C. L. Eglin as Vice-president of the Institute by the Board of Managers was confirmed.

A report of progress was presented by the Committee on Science and the Arts.

The Chairman then announced that the next business of the meeting would be the presentation of the Howard N. Potts Medal jointly to John M. Weiss, Esq., B.S., and Charles Raymond Downs, Esq., Ph.D., for "their notable achievement in the scientific and commercial development of the catalytic vapour-phase oxidation of benzene to maleic acid and their pioneer work in developing a commercial process for changing aromatic to aliphatic compounds" and recognized Dr. H. J. M. Creighton of the Committee on Science and the Arts.

Doctor Creighton said, "*Mr. President:* After careful and thorough investigation, the Institute's Committee on Science and the Arts recently recommended the award of the Howard N. Potts gold medal jointly to Messrs.

John Morris Weiss and Charles Raymond Downs, for their notable achievement in the scientific and commercial development of the catalytic, vapour-phase oxidation of benzene to maleic acid, and for their pioneer work in the development of a commercial process for changing aromatic to aliphatic compounds. This medal, as you know, Sir, is awarded by the Institute for important development of previous basic discoveries, and for inventions or products of superior excellence or utilizing important principles. In the opinion of the Committee on Science and the Arts, the process invented by Messrs. Weiss and Downs more than fulfils the requirements for the award of this medal.

"In the principle, the process is simple, and consists in passing a predetermined mixture of benzene vapour and air over a heated catalyst, by the aid of which the benzene nucleus is split and changed to maleic anhydride which is subsequently converted into maleic acid by absorption in water. In reality, the catalytic, vapour-phase oxidation presents many difficulties, owing to the large number of factors affecting the reaction. These difficulties have been overcome successfully by Messrs. Weiss and Downs.

"Formerly, maleic acid was a laboratory curiosity costing five dollars an ounce; now, it is manufactured by the Weiss and Downs process in large quantities at a low price. Most of this acid is transformed to malic acid, a food product which is used to replace the more expensive citric acid; but, when the low cost and very reactive nature of maleic acid are considered, there is opened up for the future the possibility of numerous, pure organic syntheses, and the commercial production of many straight chain acids hitherto obtainable only from expensive natural sources.

"I have the honour to present to you, Sir, Mr. Weiss, joint inventor of the catalytic process for the vapour-phase oxidation of benzene, who has come here this evening to receive the Howard N. Potts gold medal on behalf of Doctor Downs and himself."

The Chairman then presented the medals and accompanying documents to Mr. Weiss, who thanked the Institute for the high honor conferred upon him and his associate.

The Chairman then introduced Dr. Arthur L. Day, Director of the Geophysical Laboratory, Carnegie Institution of Washington, who presented the paper of the evening on "The Study of Earth Movements in California."

The speaker pointed out that there appears to be a better opportunity for the study of earth movements in considerable variety in California than in any other locality, except Japan. It is a region of complex geologic structure and great difference of elevation (loading) resulting in gravitation anomalies and land slips of considerable magnitude. It is proposed to study these (1) through astronomical observations of latitude for the detection of crustal creep, (2) through accurate triangulation and precise levels for the determination of local surface movements, (3) through special seismometric apparatus now building for the determination of sub-surface movement, including the place of origin of earthquake tremors, their direction of propagation and magnitude with reference to the existing faulting, (4) the location of major fault scarps off the coast which may contribute to these movements. The investigations which will cover a period of years will be conducted by the Geo-

physical Laboratory, the United States Geological Survey and the United States Coast and Geodetic Survey.

After brief discussion, a rising vote of thanks was extended to the speaker. Adjourned.

R. B. OWENS,
Secretary.

COMMITTEE ON SCIENCE AND THE ARTS.

(Abstract of Proceedings of Stated Meeting held Wednesday, October 4, 1922.)

HALL OF THE INSTITUTE,
PHILADELPHIA, October 4, 1922.

DR. H. J. M. CREIGHTON *in the Chair.*

The following reports were presented for final action:

No. 2790: Automatic Cashier. The Edward Longstreth Medal to Mr. Edward J. Brandt of Watertown, Wisconsin.

No. 2796: Noiseless Typewriter. The Edward Longstreth Medal to The Noiseless Typewriter Company of New York.

R. B. OWENS,
Secretary.

MEMBERSHIP NOTES.

ELECTIONS OF MEMBERSHIP.

(Stated Meeting, Board of Managers, October 11, 1922.)

RESIDENT MEMBERS.

MR. WILLIAM N. LEIGHNINGER, 1123 Harrison Street, Philadelphia, Pennsylvania.

NON-RESIDENT.

MR. JOSEPH F. GREENE, Kimble Glass Company, Vineland, New Jersey.

CHANGES OF ADDRESS.

MR. E. G. BASHORE, The Texas Company, Port Arthur, Texas.

MR. HERBERT S. BERLINER, Compo Company, Ltd., 131–18th Avenue, Lachine, Canada.

MR. GEORGE L. BOURNE, The Superheater Company, 17 East 42nd Street, New York City, New York.

MR. R. L. BRINTON, 3700 Kensington Avenue, Philadelphia, Pennsylvania.

MR. A. CHRISTIANSON, P.O. Box 877, Butler, Pennsylvania.

MR. CLARENCE E. CORNELIUS, 162 West Coulter Street, Germantown, Philadelphia, Pennsylvania.

MR. PATRICK B. DELANY, South Orange, New Jersey.

MR. FRANCIS X. DAILY, 109 St. Pauls Road, Ardmore, Pennsylvania.

MR. WALSTEIN F. DOUTHIRT, 1752 Equitable Building, New York City, New York.
MR. ROLFE E. GLOVER, JR., 2435 West Eighteenth Street, Wilmington, Delaware.
MR. WILLIAM H. HARDING, 1736 Land Title Building, Philadelphia, Pennsylvania.
MR. ROY LINDEN HILL, Atlas Powder Company, Tamaqua, Pennsylvania.
MR. E. E. KELLER, Hotel Sagamore, Rochester, New York.
MR. C. T. MACK, 1208 Decatur Street, N. W., Washington, D. C.
MR. J. W. WALKER, Devon, Pennsylvania.
MR. WM. R. WARNER, JR., "Sulgrave," Malvern P. O., Chester County, Pennsylvania.

NECROLOGY.

Mr. W. N. Best, 11 Broadway, New York City, New York.
Mr. Louis H. Eisenlohr, 932 Market Street, Philadelphia, Pennsylvania.
Mr. F. P. Howe, 242 South 17th Street, Philadelphia, Pennsylvania.
Mr. Henry D. Justi, 32nd and Spring Garden Streets, Philadelphia, Pennsylvania.
Mr. A. Robinson McIlvaine, Fifteenth and Hamilton Streets, Philadelphia, Pennsylvania.
Mr. Emerson McMillin, Darlington Farms, Mahwah, New Jersey.
Mr. R. Quayle, 233 N. Harvey Avenue, Oak Park, Illinois.
Mr. John Rae, 4945 Larchwood Avenue, Philadelphia, Pennsylvania.
Dr. Jokichi Takamine, Equitable Building, New York City, New York.

LIBRARY NOTES.

PURCHASES.

Advisory Committee for Aeronautics.—Technical Report for the Year 1911–12.
American Pharmaceutical Association.—Year Book, Volume 9, 1920. 1922.
American Society of Heating and Ventilating Engineers.—Transactions. 1920.
Annuaire Sucrier, 1921–22. 1922.
BRAGG, SIR WILLIAM.—Electrons and Ether Waves. 1921.
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CORRESPONDENCE.

LAFAYETTE, INDIANA, Sept. 22, 1922.

TO THE EDITOR,
JOURNAL OF THE FRANKLIN INSTITUTE,
PHILADELPHIA, PENNSYLVANIA.

DEAR SIR:

In my article on "Commutation in Continous Current Dynamos," published in the JOURNAL OF THE FRANKLIN INSTITUTE of May, 1922, reference is made to Mr. B. G. Lamme as being "the first to put the theory of commutation in a new light...." having in mind Mr. Lamme's method of considering the cutting of the various component fluxes by the conductors during commutation, and the avoidance of the usual expressions involving the coefficients of self and mutual induction. More than this is, however, included in the theory as presented in the article, and I feel that, since many other engineers have done valuable work in elucidating the difficult problems of commutation, additional names might have been mentioned in the introductory paragraphs. This would, however, have involved considerable research and care in order to avoid mistakes and the possibility of offending those whose contributions might have been overlooked or referred to with insufficient emphasis. There appears to be no doubt that the work of M. Marius Latour may be referred to without reference to other noted investigators, because so long ago as 1901-1902 he maintained against considerable opposition that if the average e.m.f. generated in the armature coil during short-circuit is to be zero, the total resultant flux linking with the coil at the end of commutation must be the same in amount as at the beginning of commutation, and this is, in effect, the fundamental principle underlying the method which is followed in my article.

Very truly yours,
(Signed) A. STILL.

BOOK NOTICES.

LEFAX RADIO HANDBOOK, by Dr. J. H. Dellinger, Chief, and L. E. Whittemore, Alternate Chief, Radio Laboratory, U. S. Bureau of Standards, Washington, D. C. Chapters I to VI inclusive. 12mo leather binding. Philadelphia, Lefax, Incorporated, 1922.

By employing a loose-leaf binder, characteristic of the Lefax Service, the publishers have issued a handbook which may be kept continuously revised as improvements in radiophony warrant the publication of supplementary matter. For a subject yet in an inchoate state and which is undergoing urgent research, a handbook of this character is to be preferred for the early literature of the art that is evolving out of the furore that marked the advent of radiophony.

There is no longer doubt whether a serious art is in formation, or a fad is being exploited commercially. The results already obtained are so intimate with the public that radiophony will presently be as essential as telephony. Though the whole subject is beset with elements of great uncertainty and complexity, and great limitations of its possible use are already evident, there

remains a demonstrated popular demand for this means of communication in addition to its remarkable technical applications.

Commercially the research and experimental resources of the electrical industry are being employed for the development of radiophony more extensively than they have ever been devoted to a distinct subject; and these technical efforts are being supplemented by experimental labors in collegiate and individual laboratories.

Coëxistent with this development, transmitting stations are not only fast multiplying in number, but many are becoming elaborately expensive in their installation, and pretentious in the programs they broadcast.

For the general public radio communication may always mean the radiophony which may be popularly employed, or short-wave communication at vocable frequency; while high-frequency radio may always be called wireless telegraphy. It is to be feared that the handbooks for radio instruction will even lessen this discrimination, rather than emphasize it, as the present work is called simply "Radio Handbook." Yet in the near future it is possible that impulse-radio may become perfected to the exclusion of high-frequency communication on a code.

The popular fad, which the recent practical advent of radiophony has produced, has already its roll of amateurs of large and increasing numbers, whose zeal causes them to plunge boldly into the most complex of the esoteric subjects of physics, where those learned in such matters proceed with caution and even trepidation.

The commercial advertising and propaganda of this subject by great and small manufacturers of its apparatus, far from clarifying the situation, is raucously increasing the scientific confusion. The catalogues of such supplies read like the old books of alchemy, and are reminders of the medical charlatanry of the Middle Ages. One stands aghast at the magniloquent and occult trade names under which simple apparatus are exploited. Advertising psychology has been practiced here with an unscrupulous hand; a subject too abstruse and complex for amateurs' manipulation is by these means vexed with needless obscuration.

In addition the public prints have instigated the amateur to purchase materials and collaborate these into a receiving set whose scheme of connections he may vary at his whim. Even attempts at transmission are recklessly encouraged. While in some instances this propaganda is permissible, the amateur generally should be warned not to attempt the construction or collaboration of a radio set, but purchase an approved outfit according to his means and choice. The influence of induction, and especially of capacity, is so subtle and baffling to control, that the most practiced experimenter must proceed here with difficulty and much uncertainty.

The literature of radiophony has multiplied with as vigorous fertility as the apparatus; inevitably much of it is poor, if not misleading. The demand for an adequate and authoritative handbook is only made more urgent through this insistence of the prints, and the "Radio Handbook," by Dellinger and Whittemore, is one of the few which may be followed with confidence by the layman or amateur. Though unpretentious in size, in its six chapters the

authors have traversed the elementary principles of this form of radio communication in a manner that is generally clear, and almost non-mathematical.

There are a few obvious omissions in it which subsequent editions should supply. The layman wants at the very outset to know how electrical transmission occurs through space. In attempting to explain this the authors have been not only unnecessarily brief, but confusing and contradictory. Though the hypotheses of the mechanism of an electro-magnetic wave-system are wholly fictitious, it is necessary in such handbooks to present in an elementary way the generally accepted fiction of an electro-magnetic wave. It is worth while to attempt to formulate this out of its heterogeneous mathematical suppositions, and obtain a comprehensible graphical representation of a wave-system of this nature.

A similar attempt should be made, assisted by a proper graphic, to explain why the electric displacement element of the electro-magnetic wave can produce a cumulative effect on the convolutions of a coil antenna, while the generating lines of magnetic force cause a zero potential in the coil by the induction of opposing e.m.fs. within it. This would afford at once an explanation for the end-on directive action of a coil antenna.

Evidently by an oversight the misleading statement is made in Chapter V that, "radio circuits consist of two elements, called capacity and inductance." The proper phrasing of this matter is essential and the error should be corrected promptly.

There is need at this juncture for a general term to designate such apparatus as is variously called a "chopper," modulator, or interrupter. Probably the term impulser would be more inclusive than any yet employed. Precisely an impulser would be an instrument to superpose upon the transmitting wave-train the impulses of audible, or vocable, frequency.

WILBUR M. STINE.

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS. Report No. 129. Aeronautic Instruments—V—Power Plant Instruments, by the Aeronautic Instruments Section, Bureau of Standards. 72 pages, illustrations, quarto. Washington, Government Printing Office, 1922.

Report No. 129 of the Committee in five parts, covers the general field of power plant instruments.

Part I gives a fairly complete discussion of all the various types of airplane tachometers studied at the Bureau of Standards. French, German, and American chronometric tachometers are described in detail; also several types of foreign and domestic centrifugal tachometers.

Part II describes in detail the apparatus and methods of testing airplane tachometers at the United States Bureau of Standards. Also, the average results of tests on many instruments of the chronometric, centrifugal, magnetic, and air viscosity type are given and are discussed.

Part III describes the principal types of distance reading thermometers for aircraft engines, including an explanation of the physical principles involved in the functioning of the instruments and the proper filling of the bulbs.

Part IV discusses briefly the use of air and oil pressure gages on aircraft, and describes the construction of various American, British, and German gages.

Part V discusses the principal gasoline depth gages now in use and gives a general summary of the advantages and disadvantages of each type. A brief description is also given of two typical flowmeters.

Report No. 141. Experimental Research on Air Propellers—V, by W. F. Durand and E. P. Lesley. Leland Stanford Junior University, California. 82 pages, illustrations, quarto. Washington, Government Printing Office, 1922.

In the previous reports on experimental research on air propellers, by W. F. Durand and E. P. Lesley, as contained in the National Advisory Committee for Aeronautics reports Nos. 14, 30, and 64, the investigations were made progressively and each without reference to results given in preceding reports and covering only information relating to forms perhaps adjacent in geometrical form and proportion. The present report is a review of the entire series of results of the preceding reports with a view of examining through graphical and other appropriate means the nature of the history of the characteristics of operation as related to the systematic variation in characteristics of forms, etc., through the entire series of such characteristics. In reviewing the results a check was made of doubtful points by repetition of tests, to remove inconsistencies where found, and generally to develop for the series of models represented by these tests a consistent set of results as judged by the relation of those for any one model to those for all models adjacent in geometrical form and proportion. The report presents the results of this general analysis and review of the previous series of experimental observations. There is also added a series of nomographic diagrams for the rapid graphical solution of the problems such as are considered in the report. The diagrams have been prepared for both metric and English units.

A SHORT HANDBOOK OF OIL ANALYSIS. By Augustus H. Gill, S.B., Ph.D., Massachusetts Institute of Technology. Revised 10th edition, 223 pages, 12mo. Philadelphia and London, J. B. Lippincott Company, 1922. Price $2.50.

The fact that ten editions of this work have been issued in a quarter of a century testifies sufficiently to its merits and accuracy. The work has been so well known for many years that no specific praise is needed. It is essentially a manual for those beginning work in this field. The author has kept this purpose in view, and hence has wisely refrained from increasing materially the size of the book by incorporating any considerable part of the great amount of new matter that has of late been added in the field of oils, vegetable, animal and mineral. The changes in the present edition are the addition of a section on examination of motor gasoline and a description of the MacMichael Absolute Viscometer. The author thinks that modifications will be later needed in both these descriptions and they are placed provisionally in an appendix. Printed in compact form and descriptions condensed, but still quite clear, the book contains a large amount of matter on a subject of great importance to all concerned in chemical or mechanical industries.

HENRY LEFFMANN.

VAN NOSTRAND'S CHEMICAL ANNUAL. A Handbook of Useful Data for Analytical Manufacturing and Investigating Chemists, Chemical Engineers and Students. Edited by John C. Olsen, A.M., Ph.D., assisted by T. R. LeCompte, B.A., M.S. Fifth issue, 1922. 886 pages and index, small 8vo. New York, D. Van Nostrand Company, 1922. Price $4.00 net.

This work has been known and used by chemists and correlated workers for eighteen years, and requires no encomiums from the reviewer. Such compilations are of great value to all engaged in laboratory or manufacturing operations. The data that have been accumulated concerning the properties of substances are scattered through thousands of publications many of which are inaccessible to the mass of chemists, and the bringing of these together in a convenient form is a most useful service. Of course, the value of such a work will depend largely on the thoroughness with which the literature is searched and the care taken in the selection of material. These requirements have been fully met in the book in hand. Many tables are given and also much descriptive matter. The list of new books covers over eighty pages, including some recent publications in France and Germany. The sizes and prices of those printed in English are given which is an accommodation. In some cases, however, it seems that books not really "new" are noted. Meldola's "Chemistry of Photography," dated 1889, is listed. This can hardly be called a "new book," and while it was a valuable and useful work in its day, it is essentially out of date, in view of the progress that has been in photographic procedure. It is true that some of the fundamental problems of photography, such as that of the latent image, are still obscure, but many new methods have come into use since 1889, and a work on the chemistry of photography should cover these.

The Annual is excellently printed with good type and paper and bound so that it lies open at almost any page.

HENRY LEFFMANN.

CHEMICAL ENGINEERING CATALOG 1922. Seventh annual edition, 1183 pages, 4to, flexible cover. New York, The Chemical Catalog Company, Inc., 1922. Price $10.00 net.

This comprehensive volume is the official standard work of reference for all those concerned in the establishment and operation of the chemical industries, and industries in which chemical processes are incidentally a feature. The growth of industries involving the application of chemical or physico-chemical methods has been enormous in the last quarter of a century and the indications are that it will continue at an increasing ratio. The volume is issued annually under the supervision of a committee composed of members of the American Institute of Chemical Engineers, the American Chemical Society and the Society of Chemical Industry, but these committeemen have no financial interest in the work, merely giving time and attention to it in the interest of the purposes for which it is printed.

A work of this character is always useful, in fact, indispensable to the satisfactory development of a nation's industries, but it is especially useful at the present time when the needs of developing American chemical industries

are so urgent. A somewhat unusual plan has been adopted of providing for the leasing of the book instead of selling it, the fee for such lease being very trifling. The privilege is, however, limited to certain classes; to those not in such groups, the work is sold outright.

The preface contains a great deal of information concerning the distribution of the work and among other matters it is stated that 11,000 copies of the present edition have been distributed. By furnishing to all firms that carry space a printed list giving the names and addresses of those to whom the book is distributed the value of the compilation is greatly increased. The book is really a wonderful compilation. It is, of course, abundantly illustrated, and being printed on fine paper with clear type and with excellent taste in the display portions, it constitutes a most interesting demonstration of the high degree of efficiency and extensive specialization that the mechanical and chemical interests have undergone. The binding is flexible and permits the book to lie open flat at any page.

HENRY LEFFMANN.

PUBLICATIONS RECEIVED.

The Origin of Spectra, by Paul D. Foote, Physicist, U. S. Bureau of Standards, and F. L. Mohler. American Chemical Society Monograph Series. 250 pages, illustrations, plates, 8vo. New York, The Chemical Catalog Company, 1922. Price $4.50.

The Mechanism of Lubrication. A popular explanation of the principles of lubrication as developed mathematically by Reynolds and Michell, and employed by the latter in the design of the well-known Michell Thrust and Journal Bearings, by William Stone, late Chief Electrical Engineer, Victorian Government Railways. Melbourne, "Industrial Australian and Mining Standard," 1922. Price 2 shillings, 9 pence.

U. S. Bureau of Mines: Bulletin No. 199, Experimental Production of Alloy Steels, by H. W. Gillett and E. L. Mack. 81 pages, plates, 8vo. Technical Paper 290, Inclusions in Aluminum-Alloy Sand Castings, by R. J. Anderson. 25 pages, plates, 8vo. Washington, Government Printing Office, 1922.

Outlines of Theoretical Chemistry, by Frederick H. Getman, Ph.D. Third edition, thoroughly revised and enlarged. 625 pages, illustrations, 8vo. New York, John Wiley and Sons, Inc., 1922.

Van Nostrand's Chemical Annual. A hand-book of useful data for analytical, manufacturing and investigating chemists, chemical engineers and students. Edited by John C. Olsen, A.M., Ph.D. Fifth issue, 1922. 900 pages, plates, portrait, 12mo. New York, D. Van Nostrand Company, 1922. Price $4.00 net.

A Short Handbook of Oil Analysis, by Augustus H. Gill, S.B., Ph.D. Revised tenth edition. 223 pages, illustrations, 12mo. Philadelphia, J. B. Lippincott Company, 1922.

Mechanical Laboratory Methods. The testing of instruments and machines in the mechanical engineering laboratory and in practice by Julian C. Small-

wood. Third edition, revised and enlarged. 423 pages, illustrations, 12mo. New York, D. Van Nostrand Company, 1922. Price $3.50 net.

National Advisory Committee for Aeronautics: Technical Notes, No. 110, The Effect on Rudder Control of Slip Stream Body, and Ground Interference by H. I. Hoot and D. L. Bacon. 7 pages, illustrations, photograph, quarto. No. 112, The N.A.C.A. Three-component Accelerometer by H. J. E. Reid. 6 pages, illustrations, photograph, quarto. No. 113, Report on the General Design of Commercial Aircraft by Edward P. Warner. 19 pages, illustrations, quarto. No. 114, Supplementary Report of Oil Scraper Piston Rings by H. S. McDewell. 8 pages, quarto. Washington, Committee, 1922.

U. S. Department of Agriculture: Department Circular 226, White-pine Blister Rust in the Western United States. Contribution from the Bureau of Plant Industry. 7 pages, illustrations, colored plates, 8vo. Washington, Government Printing Office, 1922.

Sound Absorption Measurements. PAUL E. SABINE. (*Phys. Rev.*, April, 1922).—It will be recalled that Professor Sabine of Harvard measured the absorbing power of sound waves of unit areas of various substances. Beneath his calculations lay the assumption that the total absorbing power of a number of articles, such as an assemblage of cushions, was in proportion to their total area. This now seems to lack justification at least in the case of highly absorbent materials. For these the apparent absorbing power per unit area appears to depend on the area and shape of the sample tested as well as upon its position in relation to other absorbing surfaces, provided the dimensions of the sample are not large with respect to the wave-length of the sound employed. With felt the absorbing power of each square metre grew less as the total area of the material exposed in the Sound Chamber of the W. C. Sabine Laboratory was made greater. Long narrow pieces manifested a larger absorbing power per unit area than equal areas in the form of a square, the ratio in the most striking case being about 3 : 1. It may be that diffraction has no inconsiderable part in such effects. G. F. S.

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